

THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 28

JUNE, 1943

No. 6

PARKERITE ($\text{Ni}_3\text{Bi}_2\text{S}_2$) FROM SUDBURY, ONTARIO: REDEFINITION OF THE SPECIES¹

C. E. MICHENER,

*The International Nickel Company of Canada, Limited,
Copper Cliff, Ontario*

AND

M. A. PEACOCK,

University of Toronto, Toronto, Canada.

ABSTRACT

Parkerite is orthorhombic with the probable space-group $Pmm\ 2-C_{2v}^1$. The unit cell with $a=4.02$, $b=5.52$, $c=5.72$ Å, contains $\text{Ni}_3\text{Bi}_2\text{S}_2$. Found only in grains and cleavage fragments, tabular on (001) and striated or stepped parallel to $[\bar{1}10]$ by prevalent lamellar twinning on (111). Cleavage (001), perfect. Parting (111). Fracture uneven. Brittle. Hardness 3 (B+). Specific gravity 8.4 (meas.), 8.50 (calc.). Colour, bright bronze, tarnishing darker. Lustre metallic. Streak black, shining. Opaque. Non-magnetic. Good electrical conductor. Polished sections light cream coloured, noticeably pleochroic, strongly anisotropic, showing lamellar twinning. Composition $\text{Ni}_3\text{Bi}_2\text{S}_2$, requiring Ni 26.7, Bi 63.6, S 9.7 = 100. Analysis: Ni 26.8, Bi 63.6, S 9.2, Pb trace = 99.6. Soluble in concentrated HNO_3 . Strongest x-ray powder lines: (10) 2.85, (9) 2.33, (7) 1.645 Å. Occurs sparingly embedded with galena, sulphides, arsenides, and tellurides, in the extremities of one of the ore-bodies in the Sudbury district, Ontario. Obtained in crystalline masses by fusing the elements in nitrogen or in a vacuum.

Although the original description of parkerite from South Africa (Scholtz, 1936) is too indefinite to permit an exact comparison, the Sudbury mineral can be identified with parkerite on the basis of x-ray powder data.

A recent study of the ore minerals of the Sudbury area (Michener, 1940) revealed more than thirty species containing a considerable variety of metallic elements. Of particular interest was the prevalence of the element bismuth which enters the composition of several of the observed minerals. One of these bismuth minerals was noticed in polished sections as a pale cream coloured mineral with strong anisotropism and striking lamellar twinning in almost every section. On further study this mineral proved to be a nickel bismuth sulphide which could not be identified with any described species.

The unknown mineral was later received by the second author for

¹ Published with the permission of The International Nickel Company of Canada, Limited.

further examination. As the work progressed it was noted at Copper Cliff that the unknown mineral might be parkerite (Scholtz, 1936), an imperfectly known mineral tentatively described as a new nickel sulphide from the nickel ores of South Africa. A closer comparison of the properties of the Sudbury mineral with the description of parkerite, to be given later, showed that there can be no reasonable doubt of the identity of the two minerals, even though our mineral contains 63.6 per cent of bismuth which appears to have been overlooked in parkerite. Although the introduction of a new name might be justified under these circumstances we have decided to retain the name parkerite and offer the present account as a redefinition of the species.

This joint work was done in co-operation with Dr. A. B. Yates, Chief Geologist, and Dr. G. A. Harcourt, Acting Superintendent of Research, of The International Nickel Company at Copper Cliff, Ontario. Dr. F. G. Smith, formerly at the University of Toronto and now at the Geophysical Laboratory, Washington, D. C., made an important contribution to the work done in Toronto, by preparing synthetic parkerite which not only provided abundant material to compare with the scanty mineral, but indicated the exact composition which was subsequently confirmed by a new analysis of the mineral. The mineral was recognized and isolated at Copper Cliff where the physical and chemical properties were determined; the crystallographic and synthetic work and some confirmatory and supplementary observations were carried out in Toronto, where the present account was prepared from the assembled information. In this way we have obtained a full description which is largely verified by independent observations.

Since natural and artificial parkerite are alike in all their specific properties it will be of interest to give parallel descriptions of the two materials before giving an account of the preparation of the synthetic compound.

OCCURRENCE

Parkerite is found in small stringers and veinlets in the extremities of the ore-body in one of the Sudbury mines,² where it occurs sparingly in association with galena, native bismuth, bismuthinite, tetradymite, hes-site, cubanite, maucherite, niccolite, sperrylite, and gold, together with the prevailing chalcopyrite, pyrrhotite, and pentlandite. The association with galena is particularly persistent and characteristic. As a group these minerals occur around the margins of the main copper-nickel-iron sulphides; parkerite has not been found in the central part of any of the larger sulphide masses.

² Under present conditions we are not permitted to define the locality more closely.

PREPARATION OF MATERIAL

Parkerite occurs in grains rarely larger than 1 mm. in diameter. A sample of the mineral was obtained by a combination of methods. Samples of the ore containing parkerite were crushed and sized to a 65-100 mesh fraction and concentrated on the Haultain superpanner, which gave a product consisting largely of galena, with parkerite, pyrrhotite, and chalcopyrite. From its behaviour on the superpanner parkerite appeared to have a specific gravity similar to that of galena. Most of the galena was removed from this concentrate by depressing it in a flotation cell; the magnetic pyrrhotite was taken out with a magnetic separator; and the chalcopyrite and gangue were separated with Clerici solution. The concentrate thus obtained consisted largely of parkerite, with some galena, non-magnetic pyrrhotite, niccolite, and pentlandite. These impurities were removed with dilute nitric acid in which parkerite is insoluble. The resulting concentrate, still showing grains of gold and sperrylite, was finally cleaned by hand.

PHYSICAL PROPERTIES

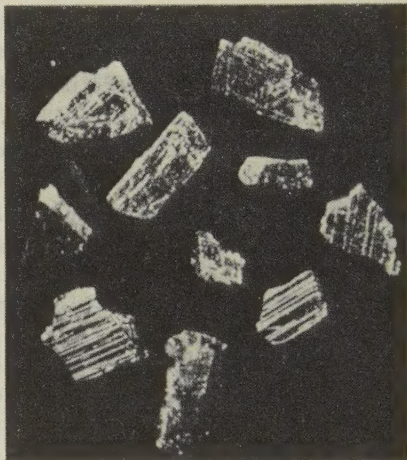
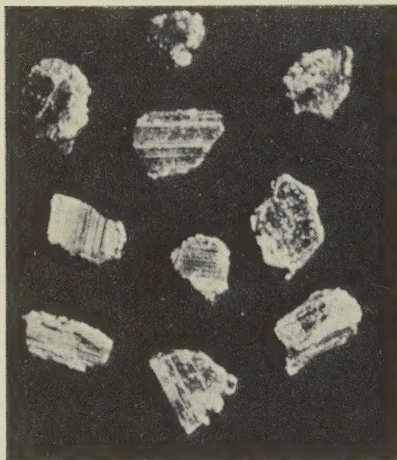
Single grains of parkerite (Figs. 1 and 3) are bright bronze coloured with brilliant metallic lustre on fresh fractures, becoming darker and dull on tarnished surfaces. There is an eminent cleavage in one direction and a good parting parallel to the twin lamellae which intersect the perfect cleavage in one or two directions, giving plates bounded by parallel edges or rhombic outlines. The mineral is brittle, with an uneven fracture, and it gives a black shining streak, barely marking paper. The hardness is 3 and the specific gravity is 8.4, measured by F. G. Smith with the Berman balance, on a few milligrams of selected grains. The mineral is non-magnetic and a good conductor of electricity.

Fragments of artificial parkerite (Fig. 2) are slightly brighter and more sharply crystallized than the natural material but otherwise indistinguishable from the mineral. On larger samples the specific gravity is 8.44 (Smith), 8.43 (Peacock).

In polished sections (Fig. 4) parkerite appears in shapeless areas with a light cream colour that contrasts sharply with that of adjoining galena. Reflection pleochroism is perceptible and the anisotropism is strong, greenish-grey to yellowish-brown, even slate-blue to salmon-pink, depending on the adjustment of the nicols. Crossed nicols almost invariably show strong twin lamellae in one direction, usually traversed obliquely by weaker lamellae. The hardness is B+, as indicated by a needle-scratch traversing galena, parkerite, and chalcopyrite, under uniform pressure. Etch reactions: HNO_3 , blackens instantly; HCl , negative;

KCN, negative; FeCl_3 , blackens instantly; KOH, negative; HgCl_2 , stains iridescent.

A polished section of the artificial product (Fig. 5) shows a coarse mosaic of grains differing in no significant way from those of the mineral. The twin lamellae in the synthetic product are sharp and narrow and the second direction is almost equally well developed, indicating that the two directions may be crystallographically equivalent.



FIGS. 1, 2. Parkerite: fragments of natural and artificial crystals striated or stepped in one or two directions by lamellar twinning. Inclined illumination and equal magnification; the largest fragment is 1.4 mm. long. Fig. 1 (left), natural fragments. Fig. 2 (right), artificial fragments.

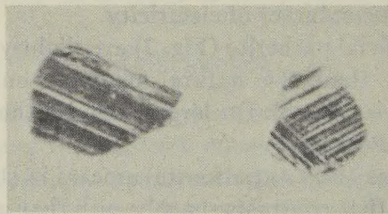
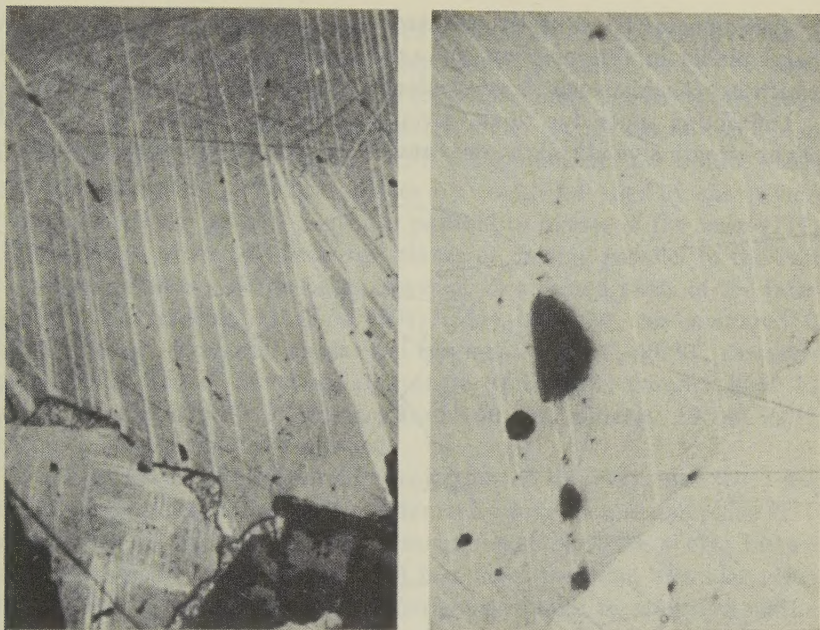


FIG. 3. Parkerite: natural fragments. Ring illumination; the larger fragment is 0.9 mm. long.

CRYSTALLOGRAPHIC PROPERTIES

Unit cell. For the determination of the symmetry and lattice dimensions of parkerite the following x-ray photographs were taken on a



FIGS. 4, 5. Parkerite: polished sections of natural and artificial materials showing strong anisotropism and twin lamellae in two directions. Vertical illumination, crossed nicols, and equal magnification; each field is 1.17×0.73 mm. Fig. 4 (left), natural material. Fig. 5 (right), artificial material.

cleavage fragment (0.2 mm.) of the mineral, with copper radiation: rotation about the axis $[\bar{1}10]$ (edge between the perfect cleavage and the parting), and Weissenberg resolutions of the zero, first, and second layer-lines; rotation about the axis $[001]$ (normal to the perfect cleavage), and Weissenberg resolution of the zero layer-line. A series of single crystal photographs were also taken on a cleavage fragment of the artificial compound: rotation about $[001]$ and Weissenberg resolutions of the zero, first, and second layer-lines; and rotation about $[100]$ with Weissenberg resolution of the zero layer-line.

Corresponding photographs of the natural and artificial compounds are alike in the positions and relative intensities of the spots. The films taken with $[001]$ as the rotation axis show orthorhombic symmetry and measurements on the films from the mineral fragment give the cell dimensions:

$$a = 4.02, b = 5.52, c = 5.72 \text{ \AA}$$

which yield the ratios:

$$a:b:c = 0.7283:1:1.0362.$$

This mineral is naturally oriented with the perfect cleavage as the basal plane; in this position the axis normal to the perfect cleavage, which is probably polar, is conveniently vertical.

Diffraction spots due to the twin lamellae were recognized by their slight progressive displacement and lack of orthorhombic symmetry

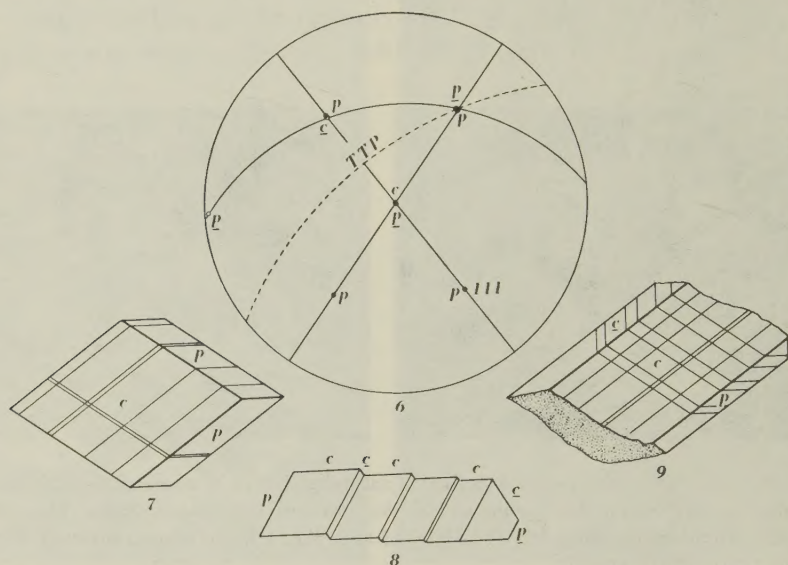


FIG. 6. Parkerite: stereographic projection of $c(001)$ and $p(111)$ twinned by reflection in (111) .

FIGS. 7, 8, 9. Parkerite: cleavage fragments of the artificial material, with cleavage $c(001)$ and twinning and parting on $p(111)$. The largest fragment is 0.8 mm. long. Figs. 7, 9, plan on (001) . Fig. 8, plan on the plane normal to $[110]$.

with reference to the axes of the main crystal. A general condition of spectral omission, (hkl) present only with $(k+l)$ even, is approached but not strictly realized except in the zone $[001]$, where $(hk0)$ is present only with k even. These conditions do not serve to fix the space-group, but a study of the atomic arrangement, now in progress, indicates a structure with the symmetry of the space-group $Pmm2-C_{2v}^1$ (pyramidal class— $mm2$).

The unit cell of parkerite contains one molecule of $Ni_3Bi_2S_2$, giving the calculated density 8.50, as compared with 8.4 measured on the mineral and 8.44 measured on the artificial compound.

Cleavage, parting, twinning. Fragments of natural and artificial parkerite are all twinned intergrowths consisting of tablets bounded by the

eminent basal cleavage and traversed by twin lamellae which are parallel to planes of the form (111) of the main tablet. The lamellae cut the basal plane in the directions $[\bar{1}10]$ and $[110]$ which make the calculated angle $72^{\circ}08'$, as compared with $72\frac{1}{2}^{\circ}$ measured under the microscope on a plate of the mineral, $72^{\circ}17'$ measured with the goniometer on a plate of the artificial compound. The basal plates are usually bevelled by one or more planes which are parallel or nearly parallel to planes of the form (111). These planes proved to be either planes of parting parallel to the twin lamellae, or planes of the basal cleavage on twinned parts of the intergrowth. The calculated angle (001):(111) is $60^{\circ}24'$, as compared to $60^{\circ}02'$, $60^{\circ}32'$, measured on natural fragments, $60^{\circ}24'$, $60^{\circ}30'$, measured on artificial plates. The calculated angle (001):(001) twinned is $59^{\circ}12'$ which compares with $59^{\circ}20'$ measured on the mineral, $59^{\circ}14'$ – $59^{\circ}17'$ noted on the synthetic compound.

Figure 6 gives a stereographic projection of the cleavage $c(001)$ and the parting $p(111)$ of parkerite, twinned by reflection in the plane (111) whose trace is marked TTP . The projection shows that $p(\bar{1}\bar{1}1)$ in twin position is nearly parallel to $c(001)$ in normal position, and vice versa. Professor J. D. H. Donnay has been good enough to send us a mathematical treatment of the twin law in the form developed by Friedel (1926, p. 245). According to this discussion the twin law is an example of twinning by reticular pseudomerohedry, with index 2 and obliquity $1^{\circ}35\frac{1}{2}'$. The prevalence of the twinning on this law is explained and predicted by the small values of the index and the obliquity.

Figures 7, 8, 9 show typical fragments of artificial parkerite with twin lamellae parallel to $p(111)$ and $p(\bar{1}\bar{1}1)$. Similar but less perfect forms were found among the natural fragments. No case was noted of twinning on three or four of the equivalent planes in the orthorhombic holohedry and no certain indication of the crystal class was obtained from the morphology.

CHEMICAL PROPERTIES

Parkerite is completely soluble in concentrated HNO_3 but is insoluble in HCl . A spectrographic analysis showed the presence of Ni and Bi, with slight traces of Cu and Sn; not present: Fe, Mn, W, Ti, Sc, Co, Pd, Ag, Cd, Ir, Pt, Te, As, Sb. S was revealed by a microchemical test. Quantitative analyses on small picked samples gave the values in Table 1. These were obtained by first estimating Ni (by dimethylglyoxime) and Bi (by electrolysis) on a sample of the artificial product. The values thus obtained were used to standardize the dithizone method for Ni and Bi, which was then applied to a sample of the mineral weighing 2.75 mg. S was determined on a separate sample of 30 mg.

As shown in Table 1 parkerite and the synthetic compound conform closely to the composition $\text{Ni}_3\text{Bi}_2\text{S}_2$, which appears to be a new type of mineral composition. The formula shows a resemblance to the spinel

TABLE 1

	1	2	3
Ni.....	26.8	27.42	26.7
Bi.....	63.6	64.00	63.6
S.....	9.2	—	9.7
Pb.....	trace	—	—
	99.6		100.0

1. Parkerite, Sudbury, Ontario. Microanalysis by W. Wagner.

2. Artificial parkerite. Partial analysis by W. Wagner.

3. Percentage composition of $\text{Ni}_3\text{Bi}_2\text{S}_2$.

formula, $\text{RO} \cdot \text{R}_2\text{O}_3$, but there is no suggestion of a structural relationship to this cubic type. Ullmannite (NiSbS) is also cubic, and kallilite, to which Dana (1892, p. 1039) gave the hypothetical formula NiBiS , is merely a bismuthian ullmannite (Peacock and Berry, 1940, p. 60) with the composition $\text{Ni}(\text{Sb}, \text{Bi})\text{S}$. With no close mineral relatives parkerite might be appended to the Arsenopyrite Group in a system of descriptive mineralogy.

X-RAY POWDER DATA

Parkerite gives a distinctive x-ray powder pattern which is shown in the films from natural and artificial materials reproduced without reduction in Figs. 10, 11. Table 2 gives for each line the relative intensity I estimated visually³ on a film from the natural material; the measured glancing angle $\theta(\text{Cu})$; the corresponding measured interplanar spacing d (meas.); the indices (hkl) of the reflecting lattice planes; and the calculated spacing of the reflecting planes d (calc.). For determinative purposes the columns I and d (meas.) suffice (Harcourt, 1942); the addition of θ is a convenience, while (hkl) and d (calc.) give the desirable verification of a standard powder pattern (Peacock, 1941).

The powder photographs (Figs. 10, 11) were made in Toronto with equipment which appears to give better than ordinary resolution. On films made for rapid determinative purposes some of our slightly separated lines may coalesce and some of our faint lines may not appear.

³ We estimated the intensities independently with differences which only rarely amounted to 2 degrees on a 10 degree scale.

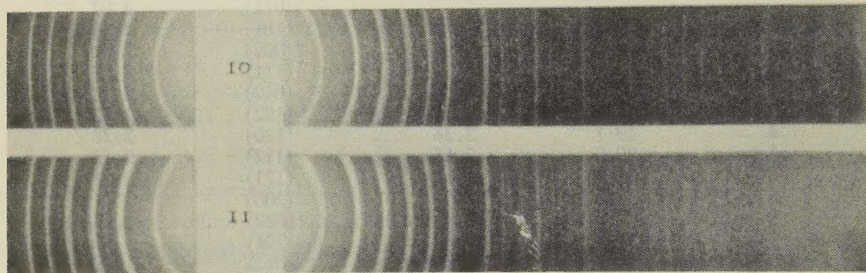
TABLE 2. PARKERITE: X-RAY POWDER SPECTRUM (Cu/Ni)

ORTHORHOMBIC; $a=4.02$, $b=5.52$, $c=5.72$ Å

<i>I</i>	θ (Cu)	<i>d</i> (meas.)	(<i>hkl</i>)	<i>d</i> (calc.)
4	7.6°	5.8 Å	(001)	5.72 Å
7	11.05	4.01	{(100)	4.02
1	13.5	3.29	{(011)	3.97
10	15.65	2.85	{(101)	3.29
1	17.5	2.56	{(002)	2.86
9	19.25	2.33	{(111)	2.83
4	19.7	2.28	{(012)	2.54
$\frac{1}{2}$	20.9	2.15	{(102)	2.33
$\frac{1}{2}$	21.3	2.12	{(120)	2.28
5	22.4	2.02	{(112)	2.15
5	22.8	1.984	{(121)	2.11
$\frac{1}{2}$	23.9	1.897	{(200)	2.01
6	25.25	1.802	{(022)	1.986
2	25.55	1.782	{(201)	1.896
$\frac{1}{2}$	26.5	1.723	{(013)	1.802
7	27.85	1.645	{(122)	1.781
$\frac{1}{2}$	28.5	1.611	{(103)	1.723
4	32.5	1.431	{(113)	1.645
5	32.9	1.415	{(202)	1.645
$\frac{1}{2}$	33.7	1.385	{(131)	1.606
3	34.85	1.345	{(004)	1.430
$\frac{1}{2}$	35.5	1.324	{(222)	1.413
2	37.25	1.270	{(014)	1.384
5	39.4	1.211	{(203)	1.383
1	40.4	1.186	{(104)	1.347
2	41.3	1.165	{(213)	1.342
1	42.4	1.140	{(033)	1.324
$\frac{1}{2}$	43.4	1.119	{(311)	1.270
4	45.5	1.078	{(024)	1.270
2	51.8	0.978	{(302)	1.213
1	54.5	0.944	{(124)	1.211
$\frac{1}{2}$	56.0	0.927	{(312)	1.185
$\frac{1}{2}$	56.4	0.923	{(141)	1.173
$\frac{1}{2}$	57.3	0.913	{(214)	1.140
1	58.6	0.901	{(015)	1.120
$\frac{1}{2}$	61.0	0.879	{(115)	1.079
$\frac{1}{2}$	61.6	0.874	{(215)	0.979
$\frac{1}{2}$	63.2	0.861	{(304)	0.978
2	69.0	0.823	{(420)	0.945
			{(135)	0.944
			{(333)	0.942
			{(106)	0.928
			{(324)	0.922
			{(116)	0.915
			{(026)	0.901
			{(126)	0.879
			{(413)	0.878
			{(235)	0.875
			{(054)	0.874
			{(342)	0.873
			{(206)	0.862
			{(315)	0.860
			{(226)	0.823
			{(404)	0.822

SYNTHESES

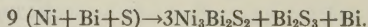
The compound $\text{Ni}_3\text{Bi}_2\text{S}_2$ was obtained in pure, coarsely crystallized masses by fusing the elements in the proper proportions in a sealed pyrex tube in which the air had been displaced by nitrogen at low pressure (Smith), or entirely removed (Burr). On gentle heating with an open



FIGS. 10, 11. Parkerite: x-ray powder photographs of natural and artificial materials with Cu/Ni radiation. Full size reproductions of contact prints (1 mm. on film = $1^\circ \theta$). Fig. 10, natural material. Fig. 11, artificial material.

flame the charge combined vigorously, giving a liquid which crystallized with the liberation of much heat after the flame was withdrawn. When broken in halves the product was found to be a solid crystalline aggregate showing brilliant continuous cleavage surfaces up to 5 mm. in width. A polished section showed that the product was pure and homogeneous.

This satisfactory result was not, however, immediately obtained, since the first purpose of the synthetic work was to check a simpler but, as it proved, incorrect formula, NiBiS , suggested by preliminary analyses. The product of a charge with this composition proved to be a mixture of parkerite, bismuthinite, and bismuth, representing the reaction:



This showed that parkerite contains relatively more Ni than NiBiS , and, incidentally, that a Bi-analogue of ullmannite probably cannot exist.

With this clue, the proper composition of parkerite was eventually found by preparing charges with the limited number of simple rational compositions permitted by the then roughly known molecular weight of the cell content and the approximate composition. Only the composition $\text{Ni}_3\text{Bi}_2\text{S}_2$ gave pure parkerite; the others showed substantial amounts of impurities. Special care was taken to exclude the composition $\text{Ni}_4\text{Bi}_2\text{S}_2$ which gave a product consisting of parkerite together with a white magnetic impurity resembling nickel.

It is noteworthy that the powder pattern of parkerite given by various impure products showed only very slight displacements of the lines as compared with the pattern of pure $\text{Ni}_3\text{Bi}_2\text{S}_2$. This showed that the compound has a very limited solid solution range.

After these experiments had been completed, and the foregoing account written, we found a reference to a published equilibrium study by Schenck and Forst (1939) bearing directly on our work. Using the established method of isothermal reduction with hydrogen, these authors studied the systems Sb-Ni-S and Bi-Ni-S. In the former system they found NiSbS (ullmannite) as the only ternary compound; in the latter system they unexpectedly found $\text{Ni}_3\text{Bi}_2\text{S}_2$ as the only ternary compound, with only a slight indication that NiBiS might appear as a metastable phase.

IDENTITY OF THE SUDBURY MINERAL AND PARKERITE OF SCHOLTZ

The name parkerite was given by Scholtz (1936, p. 186) to one of sixteen unidentified ore minerals found in the nickeliferous deposits of East Griqualand and Pondoland, South Africa. Limited material from Waterfall Gorge, Insizwa, studied in Zürich with the help of Professors Niggli and Parker, led to a description which may be condensed as follows:

Symmetry probably monoclinic, as indicated by a Laue photograph (Niggli). Composition Ni_2S_3 or NiS_2 , suggested by a partial analysis (Schilz) of a few milligrams. Cleavage in three directions, one easier than the others, giving rhomboidal plates. Polished sections creamy white, with a faint mauvish tinge, noticeably pleochroic and strongly anisotropic, always showing lamellar twinning which causes zigzag traces in sections across the best cleavage. Hardness apparently slightly less than that of galena. Negative etch-reactions only to KCN and KOH. Soluble in 50 per cent HNO_3 . Associated with galena, chalcopyrite, maucherite, sperrylite, pentlandite, niccolite, bismuth, and silicates.

Although this description lacks precision in almost all the specific characters, there is a suggestive similarity between the described appearance and associations of parkerite and those of the Sudbury mineral. However, the identity of our mineral with parkerite might not have been suspected, and certainly could not have been proved, without the x-ray powder data (Niggli) which is appended to the description of parkerite. Table 3 compares Niggli's intensities and spacings for the South African mineral with our data for the Canadian occurrence.

It will be seen that there is substantial agreement in the relative intensities and absolute spacings in the two lists. Only five of Niggli's lines

do not appear in our list. Since Niggli noted that there might be lines in his pattern due to impurities, the source of these extra lines was sought with the help of Harcourt's *Tables* (1942). Three of the extra lines (d 3.02, 1.854, 1.5905) were at once identified with the three strongest lines of chalcopyrite (d 3.03, 1.86, 1.59), leaving only two lines unidentified. Seven of our lines are missing in Niggli's list, but these are all very

TABLE 3. PARKERITE: COMPARISON OF X-RAY POWDER DATA (Cu/Ni)

Insizwa ⁴		Sudbury		Insizwa ⁴		Sudbury	
<i>I</i>	$d(\text{\AA})$	<i>I</i>	$d(\text{\AA})$	<i>I</i>	$d(\text{\AA})$	<i>I</i>	$d(\text{\AA})$
m	5.66	4	5.8	m	1.413	5	1.415
m	3.96	7	4.01	wb	1.376	$\frac{1}{2}$	1.385
.....		1	3.29	m	1.343(5)	3	1.345
m	3.02 <i>cp</i>			w	1.322	$\frac{1}{2}$	1.324
s	2.84	10	2.85	mw	1.270	2	1.270
.....		1	2.56	s	1.209(5)	5	1.211
ms	2.32	9	2.33	w	1.187	1	1.186
w	2.27(5)	4	2.28	mw	1.165	2	1.165
.....		$\frac{1}{2}$	2.15	w	1.140	1	1.140
.....		$\frac{1}{2}$	2.12	w	1.115(5)	$\frac{1}{2}$	1.119
mw	2.013	5	2.02	s	1.075	4	1.078
m	1.979	5	1.984	m	0.9788	2	0.978
w	1.897	$\frac{1}{2}$	1.897	wb	0.9440	1	0.944
mw	1.854 <i>cp</i>					$\frac{1}{2}$	0.927
m	1.792	6	1.802	m	0.9240	$\frac{1}{2}$	0.923
w	1.782	2	1.782			$\frac{1}{2}$	0.913
w	1.714	$\frac{1}{2}$	1.723	m	0.8987	1	0.901
s	1.640	7	1.645	mw	0.8912		
w	1.606	$\frac{1}{2}$	1.611			$\frac{1}{2}$	0.879
mw	1.590(5) <i>cp</i>			mw	0.8755	$\frac{1}{2}$	0.874
w	1.568			w	0.8589	$\frac{1}{2}$	0.861
s	1.427	4	1.431	mw	0.8217	2	0.823

⁴ Niggli, in Scholtz (1936, p. 188). Intensities: w, weak; m, medium; s, strong; b, broad line. *cp*, line due to chalcopyrite.

weak. The agreement is in fact better than is usually obtained on one and the same mineral by different observers using different appliances, and thus the minerals from Canada and South Africa represent a single mineral species. Lack of orthorhombic symmetry in a Laue photograph of a basal plate of parkerite would be expected, since the ever-present twin lamellae would give unsymmetrical reflections. The serious discrepancy in the chemical composition suggested by Scholtz can be attributed to lack of sufficient material for adequate chemical study.

When these conclusions were reached (November, 1941) we wrote Dr. Scholtz (Pretoria) and Professor Parker (Zürich) outlining our results and suggesting a test for essential Bi in parkerite. Up to the present time (March, 1943) we have had no reply and therefore the verification of the composition $\text{Ni}_3\text{Bi}_2\text{S}_2$ on the South African mineral must be left to the future.

REFERENCES

- DANA, E. S., *System of mineralogy*, 6th ed., New York (1892).
FRIEDEL, G., *Leçons de cristallographie*, Paris (1926).
HARCOURT, G. A., Tables for the identification of ore minerals by x-ray powder patterns: *Am. Mineral.*, **27**, 63–113 (1942).
MICHENER, C. E., Minerals associated with large sulphide bodies of the Sudbury type: *Ph.D. Thesis*, University of Toronto (unpublished) (1940).
PEACOCK, M. A., On the identification of minerals by means of x-rays: *Trans. Roy. Soc. Canada*, **35**, sec. 4, 105–113 (1941).
——— AND BERRY, L. G., Röntgenographic observations on ore minerals: *Univ. Toronto Studies, Geol. Ser.*, No. **44**, 47–69 (1940).
SCHENCK, R., AND VON DER FORST, P., Gleichgewichtsstudien an erzbildenden Sulfiden. II: *Zeits anorg. Chem.*, **241**, 145–157 (1939).
SCHOLTZ, D. L., The magmatic nickeliferous ore deposits of East Griqualand and Pondoland: *Trans. Geol. Soc. South Africa*, **39**, 81–210 (1936).

THE MINERALOGY AND GENESIS OF HYDROXYLAPATITE

LANE MITCHELL,

Department of Geology, Georgia School of Technology,

AND

G. T. FAUST, S. B. HENDRICKS, AND D. S. REYNOLDS,

United States Bureau of Plant Industry, Washington, D. C.

ABSTRACT

The mineral species hydroxylapatite has been re-examined. Two new occurrences have been found, Cherokee County, Georgia, and von der Rossa, Val Devero, Italy. The Swiss so-called "hydroxylapatite" is actually a fluor-hydroxylapatite. Physical, chemical, and mineralogical constants have been determined and in part interpreted. When sufficient hydroxyl is present in an apatite, it is reflected in the increase in refractive indices and birefringence. *Hydroxylapatite has only been found associated with talc and chlorite schists, which indicates that it is formed by metamorphism in the presence of much water and with the simultaneous formation of other minerals rich in the hydroxyl group.*

INTRODUCTION

Apatite is a very common mineral, being regarded by Clarke and Washington as one of the ten most abundant minerals in the earth's crust. Although much advance has been made in our knowledge of the mineralogy of the apatite group of minerals during the last decade, some important members of the group have not been adequately studied. It is the purpose here to deal with the mineralogy and interesting mineral association of the hydroxyl-bearing variety, hydroxylapatite.

LITERATURE AND NOMENCLATURE

In 1856, A. A. Damour¹ analyzed an apatite from the vicinity of St. Giron in the Pyrenees, which he found to contain 3.36% F and 5.30% H₂O, and to which he gave the name hydro-apatite, in allusion to its hydrous character. Schaller² examined this analysis and concluded that it corresponded to the less hydrous mineral francolite. Schaller as a result of his study of the work of Lacroix³ suggested a theoretical end-member of the apatite group, rich in hydroxyl, which he called hydroxy-apatite. This compound had been synthesized by Warrington,⁴ in 1873,

¹ Damour, A. A., Sur l'hydro-apatite, espèce minéral; *Annales des mines*, **10**, 65-68 (1856).

² Schaller, W. T., Mineralogical Notes—Series 2, *U. S. Geol. Surv., Bull.* **509**, 89-100 (1912).

³ Lacroix, A. L., Sur la constitution mineralogique des phosphorites francaises: *Compt. rend.*, **150**, 1213 (1910); *Mineralogie de la France*, **4**, part 2, 555 (1910).

⁴ Warrington, R., On the decomposition of tricalcic phosphate by water: *Jour. Chem. Soc. (London)*, **26**, 983-989 (1873).

who referred to it as hydrated oxygen apatite. The synthesis was repeated by Bassett⁵ in 1917, who used the term hydroxyapatite.

The first natural occurrence of material approaching hydroxylapatite in composition was reported by Burri, Jakob, Parker, and Strunz.⁶ They used the name "hydroxylapatit" for the naturally occurring mineral and thus established this species. "Hydroxylapatit" is universally used in the recent rather extensive German literature⁷ on the chemistry of this compound. In the English chemical literature, since the time of Bassett, the name hydroxyapatite has been used.

CRYSTALLOGRAPHY

Hydroxylapatite from the old Verde Antique serpentine quarry near Holly Springs, Cherokee County, Georgia, exhibits only a small number of forms. The best crystal observed measured 6 by 6 by 11 mm. It was elongated parallel to the c axis, and the developed forms were the prism terminated by the basal pinacoid. Natural etch figures on the prism faces and etch grooves on the basal pinacoid are sketched in Fig. 1. The etch pits on the prism faces are alike in shape and orientation and confirm the hexagonal character of the c axis. Moreover, they are divisible by one plane of symmetry parallel to the equatorial plane, and they show that a center of symmetry is present. The etch data agree with the requirements of the hexagonal dipyramidal class. The etch grooves on the base form an hexagonal pattern, the principal system of grooves being parallel to the sides of the prism while the secondary system is perpendicular to these. Honess⁸ has described similar etching produced on apatite crystals in the laboratory.

The best developed crystal of the Swiss material was 4.5 mm. long and 4.0 mm. in diameter. It consisted of a prism terminated by a bipyramid. of the same order as the prism, as well as by the basal pinacoid. This crystal was so corroded by wavy grooves as to have no value for symmetry determination.

X-ray powder diffraction photographs were made on samples of hydroxylapatites from Switzerland and Georgia. The diffraction patterns, portions of which are reproduced in Fig. 2, are similar to those obtained

⁵ Bassett, H., The phosphates of calcium. IV. The basic phosphates: *Jour. Chem. Soc. (London)*, **111**, 620-642 (1917).

⁶ Burri, C., Jakob, J., Parker, R. L., and Strunz, H., Über hydroxylapatit von der Kemmelton, bei Hospenthal, (Kt. Uri): *Schweiz Min. Petr. Mitt.*, **15**, #2, 327-399 (1935).

⁷ For a summary of the chemical literature, note Eisenberger, S., Lehrman, A., and Turner, W. D., The basic calcium phosphates and related systems. Some theoretical and practical aspects: *Chem. Rev.*, **26**, 257-296 (1940).

⁸ Honess, A. P., The Nature, Origin and Interpretation of the Etch Figures on Crystals. John Wiley & Sons, Inc., New York, p. 171 (1927).

from fluorapatite and synthetic hydroxylapatite. These patterns do not show the separation of the (121), (112), and (300) reflections found by Thewlis, Glock, and Murray⁹ which would result from changing the axial ratio from $a:c = 1.000:0.734$ to $a:c = 1.000:0.730$. These reflections might

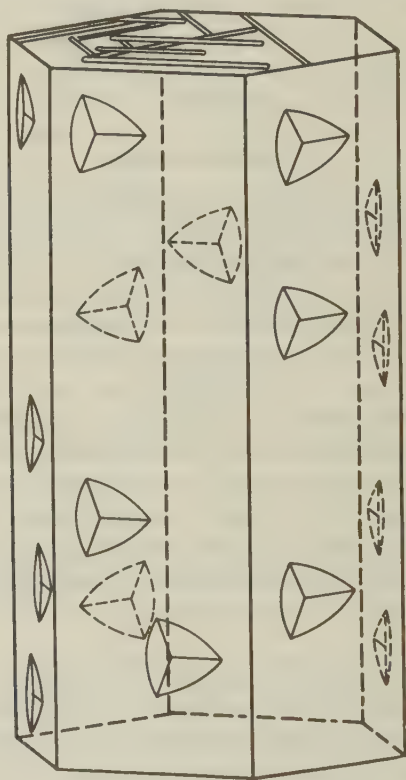


FIG. 1. Crystal forms and natural etching of the Georgia hydroxylapatite.

be slightly shifted since the lines are somewhat broadened. However, the lines at large angles from the various materials have similar spacings and intensities. Lattice dimensions of these samples of hydroxylapatite and fluorapatite, therefore, are identical within limits of experimental error. Close similarity of lattice dimensions of course is a result of the approximately equal ionic radii of F^- and $(OH)^-$.

⁹ Thewlis, J., Glock, G. E., and Murray, M. M., Chemical and x-ray analysis of dental, mineral, and synthetic apatites: *Trans. Faraday Soc.*, **35**, 358-363 (1939).

COLOR

The color of a number of the Georgian hydroxylapatites occurring in talc schists was determined by comparison with Ridgway's tables and found to range from wax yellow (21'.0—yy) to strontian yellow (23'.yel-

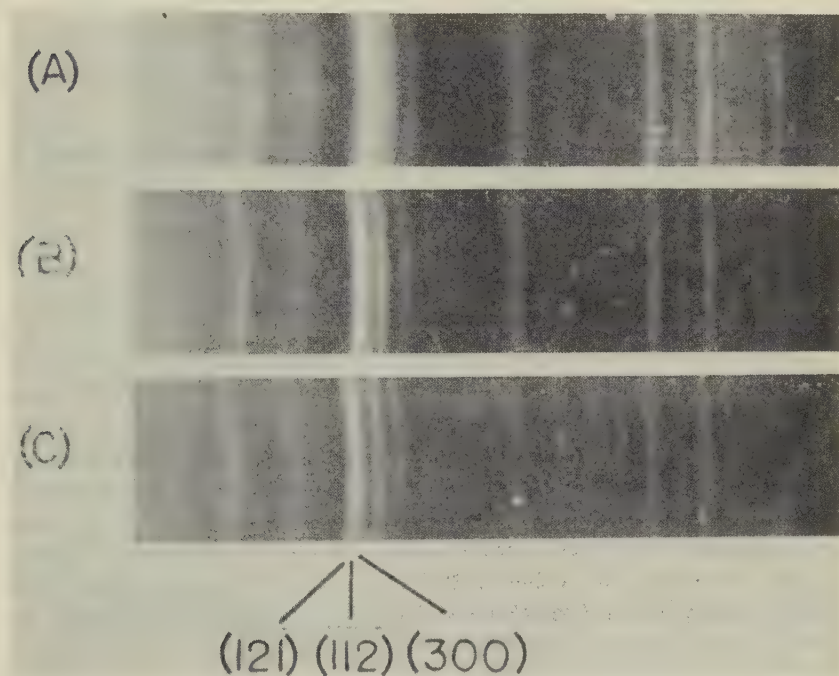


FIG. 2. X-ray powder diffraction patterns, Cu $K\alpha$ radiation, of (A) synthetic hydroxylapatite (heated for one hour at 800°C.), (B) hydroxylapatite from Georgia, (C) fluorapatite.

low). The Swiss mineral in the nomenclature of Ridgway was found to be sea-foam green (27''.g—y.f.), while synthetic hydroxylapatite is a white powder. The fluor-hydroxylapatite of the chlorite schists from Georgia ranges from deep chrysolite green (27''.g—y) to deep sea-foam green (27''.g—y.d).

OPTICS

Optical properties were determined by the immersion method using sodium light and are given in Table 1. To these values have been added the so-called "oxyapatite" of Bianchi¹⁰ and the data for fluorapatite and chlorapatite.

TABLE 1. OPTICAL PROPERTIES OF SOME APATITES

	Georgia Hydroxyl- apatite	Georgia fluor- Hydroxyl- apatite	Swiss fluor- Hydroxyl- apatite	Italian Hydroxyl- apatite	Fluor- apatite	Chlor- apatite
Uniaxial	(-)	(-)	(-)	(-)	(-)	(-)
ω_{Na}	1.651 ± 0.001	1.645 ± 0.001	1.6452	1.6507	1.633 ± 0.001	1.667
ϵ_{Na}	1.644 ± 0.001	1.640 ± 0.001	1.6413	1.6452	1.629 ± 0.001	1.664
$(\omega - \epsilon)_{\text{Na}}$	0.007	0.005	0.0039	0.0055	0.004	0.003
Observer	Faust, this paper	Faust, this paper	3urri et al. ⁸	A. Bianchi ¹⁰	D. McConnell & J. W. Gruner ¹¹ Wratten filter W-90	Larsen & Berman ¹²

Schneiderhöhn¹³ states that synthetic hydroxylapatite has indices of refraction near those of hilgenstockite, $(4\text{CaO} \cdot \text{P}_2\text{O}_5)$, $\gamma_{\text{Na}} = 1.647$, $\alpha_{\text{Na}} = 1.643$. The x-ray diffraction patterns are also similar.

The presence of hydroxyl instead of fluorine in apatite increases the refractive indices. This increase has also been observed, for like substitution, in topaz.¹⁴ This is to be expected from a consideration of the ionic refractivities of fluorine, hydroxyl, and chlorine ions for which Wasastjerna¹⁵ calculated the values 2.20, 4.68, and 8.45, respectively. This relationship between the refractive indices of apatite and the ionic refractivities of the replacing atoms is shown graphically in Fig. 3, where data for the end-members are plotted.

The sample analyzed by Bianchi appears to be an hydroxylapatite. Its refractive indices and double refraction are almost identical with the

¹⁰ Bianchi, A., Apatite di Val Devero (Ossola): *Atti. Soc. Ital., Soc. Nat.*, **58**, 306-333 (1919).

¹¹ McConnell, D., and Gruner, J. W., The problem of the carbonate-apatites: Part III, *Am. Mineral.*, **25**, 157-167 (1940).

¹² Larsen, E. S., and Berman, H., The Microscopic Determination of the Non-opaque Minerals: *U. S. Geol. Surv., Bull.* **848**, 2nd ed., (1934).

¹³ Trömel, G., and Schneiderhöhn, H., Beiträge zur Kenntnis des Systems Kalziumoxyd-Phosphorpentoxyd. Mikroskopisch optische Untersuchungen der Schmelzen: *Mitt. Kaiser Wilhelm Inst. für Eisen-Forsch.* Düsseldorf, Band **14**, 25-36 (1932).

¹⁴ Pardee, J. T., Glass, J. J., and Stevens, R. E., Massive low-fluorine topaz from the Brewer Mine, South Carolina: *Am. Mineral.*, **22**, 1058-1064 (1937).

¹⁵ Wasastjerna, J. A., Über die Refraktionsäquivalente der Ionen und den Bau der zusammengesetzten Ionen: *Soc. Sci. Fenn. Comm. Phys. Math.*, **1**, #37 (1923); also, Über den Bau der Atome und Moleküle im Licht der Dispersionstheorie: *Zeits. Physikalische Chemie*, **101**, 193-218 (1922).

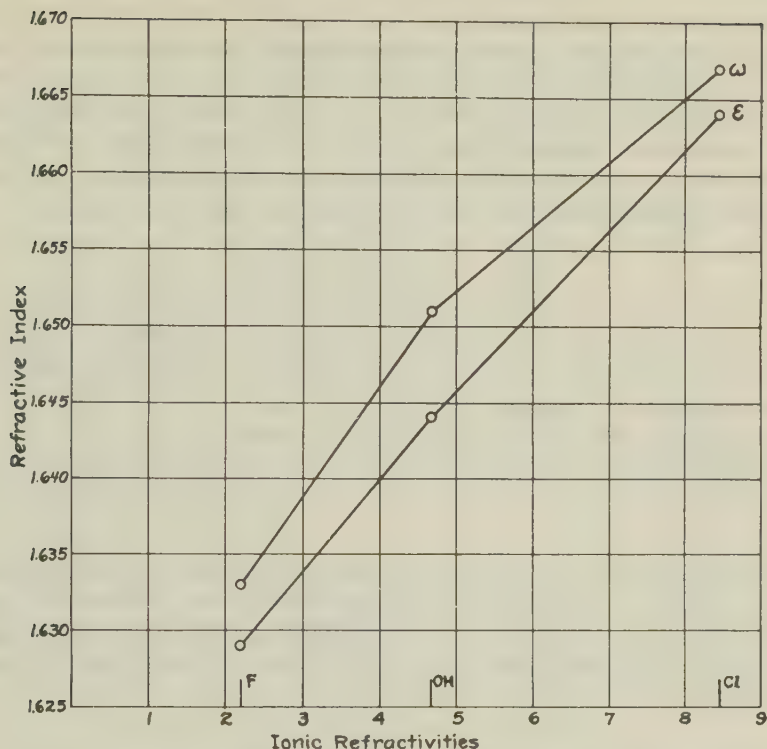


FIG. 3. Refractive indices of fluorapatite, hydroxylapatite, and chlorapatite as functions of ionic refractivities.

data obtained on the Cherokee County, Georgia, material. It could not be a mixture of chlorapatite and fluorapatite since its double refraction is roughly twice as great as either one. Although it was called an "oxyapatite" by Burri et al., the existence of such a compound is yet to be demonstrated.¹³

CLEAVAGE AND FRACTURE

The Georgia hydroxylapatite possesses a distinct conchoidal fracture whereas the Swiss mineral⁶ (poorer in hydroxyl) exhibits a fairly good cleavage parallel to the prism and an interrupted cleavage parallel to the basal pinacoid. The fluor-hydroxylapatite (Georgia), on the other hand, has a cleavage parallel to the prism. Sometimes trains of tiny inclusions occur parallel to the cleavage traces.

SPECIFIC GRAVITY

The molecular weight for the unit of structure of hydroxylapatite is 1004.69, while fluorapatite is 1008.68, a difference of only about 0.4%.

It has been previously pointed out that the lattice dimensions of the two minerals are almost indistinguishable. On the basis of these data one would necessarily conclude that the specific gravity of hydroxylapatite and fluorapatite are almost identical. The specific gravity was determined by the standard method using the analytical balance. The values obtained were corrected for the thin platinum wire-suspension and temperature. These are given in Table 2 with values from the literature.

TABLE 2. SPECIFIC GRAVITY DATA

Mineral	Locality	This Paper	Burri et al. ⁶	Larsen & Berman ⁹	Calculated*
Hydroxylapatite	Georgia	3.21	—	—	3.17
Fluor-hydroxylapatite	Swiss	3.21	3.076	—	
Fluorapatite				3.2	3.18

* $a=9.37 \text{ \AA}$, $c=6.88 \text{ \AA}$.

The value obtained by Burri et al. is surprisingly low and not in agreement with the supplementary crystal structure data. Moreover, the investigations of Kind¹⁶ on various magmatic apatites exhibiting quite a range of substitutions does not support so low a specific gravity as that reported by Burri et al.

CHEMISTRY

Analytical data

Analyses were made according to the standard methods used in the Bureau of Plant Industry for the analysis of phosphates. Fluorine was determined by a modification of the Willard-Winter method.¹⁷

The frequently used etching test for fluorine has proven to be untrustworthy and it is desirable to base statements concerning the absence of fluorine upon quantitative analyses.¹⁸

For this reason the fluorine and water contents of the Swiss material, kindly furnished by Dr. W. F. Foshag of the National Museum, were redetermined. The value for the ignition loss, namely 1.77%, checked very well with 1.73% found in the original analysis. Fluorine determina-

¹⁶ Kind, Alfred, Der magmatische Apatit, seine chemische Zusammensetzung und seine physikalischen Eigenschaften: *Chem. der Erde*, Band 12, Heft 1, 50-82 (1938).

¹⁷ Reynolds, D. S., and Hill, W. L., Determination of fluorine with special reference to the analysis of natural phosphates and phosphatic fertilizers: *Ind. & Eng. Chem.*, Anal. Ed., 11, 21-27 (1939).

¹⁸ Hillebrand, W. F., and Lundell, G. E. F., Applied Inorganic Analysis, John Wiley & Sons, Inc., New York, 595-596 (1929).

tions were, however, in complete disagreement, with 1.01% fluorine present whereas Burri et al. found none by a qualitative test. Their optical data also indicate an error in their fluorine determinations; for the birefringence and refractive indices are considerably lower than those for pure hydroxylapatite. Accordingly, the fluorine analysis from this work is used with the remainder of the analysis by Burri and his co-workers, although it is realized that the material might show considerable variation in composition.

The ignition loss of 1.73% is in excess of the expected value for an apatite containing 1.0% fluorine. Determination of water in apatites, however, is subject to exacting requirements. It is necessary to heat the sample to about 1400°C. in a current of dry air. Possible loss of halogens must be taken into account and corrections made. The material from Switzerland used in this work contains small but microscopically detectable amounts of a carbonate; a crystal dropped in cold 1:1 HCl gave slight effervescence.

Spectrographic analysis of the Georgia hydroxylapatite and fluor-hydroxylapatite, kindly made by Dr. B. C. Brunstetter and Mr. A. T. Myers of the Bureau of Plant Industry, showed that calcium and phosphorus were the major constituents; that manganese, magnesium, iron, and aluminum were present in very small amounts; and that mere traces of copper, vanadium, boron, sodium, and potassium were present.

Formulas for the several apatites computed from the data in Table 3 are summarized in Table 4. Molal values are adjusted to make the (PO_4) value exactly 6.00; which is the number of (PO_4) groups in the unit of structure of a carbonate-free apatite. The total number of positive ions, S, exceeds the theoretical value, 10.00, by about 1.5% in samples 1, 2, and 4. This might be due in part to the usual analytical error. It could also be explained by the presence of some (CO_3^{--}) groups substituting for $(\text{PO}_4)^{--}$; the 1.5% excess would require 0.4% CO_2 . Similarly the (OH, F) value exceeds 2.00, the theoretical maximum, in samples 1 and 3. This is probably due to water being occluded or adsorbed to a minor extent and not present as hydroxyl.

The material, analysis No. 4, that Bianchi described as "oxyapatite" is apparently hydroxylapatite. He failed to determine the water content—a very common error in apatite analyses. Damour's sample, No. 5, is probably fluorapatite and the large amount of water given in the analysis was evidently present as such.

Color of synthetic hydroxylapatite

Colorless hydroxylapatite can be synthesized but generally the prod-

TABLE 3. CHEMICAL ANALYSES

	1	2	3	4	5	6
	Hydroxyl-apatite. Holly Springs, Cherokee County, Georgia	Fluor-hydroxyl-apatite. Holly Springs, Cherokee County, Georgia	Fluor-hydroxyl-apatite. Kemmlerton, Hospenthal Kt. Uri, Switzerland U.S.N.N. #7708 Roebbling Coll.	Hydroxyl-apatite. Rossa, Val Devero, Italy	Damour's Hydro-apatite	Theoretical Hydroxyl-apatite
P ₂ O ₅	42.05	41.96	42.19	41.63	40.00	42.40
V ₂ O ₅	0.00	—	—	0.90 $\begin{cases} \text{Fe}_2\text{O}_3 \\ \text{Al}_2\text{O}_3 \end{cases}$	—	—
CaO	55.84	55.90	55.47	55.25	52.35	55.81
MgO	0.10	0.05	—	0.29	—	—
MnO	0.07	0.10	0.06	—	—	—
H ₂ O	1.86**	1.33**	1.73**	0.32	5.30	1.79
F	0.16	0.84	1.01	trace	3.36	—
Cl	trace	0.06	—	0.95	—	—
Insol.	0.15*	0.15*	0.60*	1.30	—	—
	100.23	100.39	101.06	100.64	101.01	100.00
Less $\begin{cases} \text{O}=\text{F} \\ \text{O}=\text{Cl} \end{cases}$	0.07	0.36	0.43	0.21	1.42	—
Total	100.16	100.03	100.63	100.43	99.59	100.00
$\frac{\text{P}_2\text{O}_5}{\text{CaO}}$			0.761		0.764	0.760
Analyst	D. S. Reynolds	D. S. Reynolds	J. Jakob ⁷ with fluorine by D.S.R.	A. Bianchi ¹¹	A. A. Damour ²	

* Insoluble in acid. Identified as talc. See Figs. 4 and 5.

** Ignition loss, corrected for small amount of fluorine volatilized.

ucts are various shades of pink. Gabriel¹⁹ first reported this observation on bone heated to redness in contact with air, which is closely related to hydroxylapatite. He thought that it might be due to the presence of rare

¹⁹ Gabriel, S., Chemical research on the mineral material of bone and teeth: *Zeits. Physiol. Chem.* **18**, 257 (1893).

earths but was unable to prove the point. Bassett⁵ observed similar pink colors in synthetic hydroxylapatite, the color varying greatly in shade and uniformity. He showed that the color could be intensified by the addition of copper salts during the course of the synthesis.

TABLE 4. OBSERVED FORMULAS OF THE VARIOUS APATITE MINERALS

Source	Formula		S	Excess Charge
1. Georgia	(Ca _{10.10} Mg _{0.02} Mn _{0.01})	(PO ₄) _{6.00} (OH _{2.09} F _{0.08})	10.13	0.09
2. Georgia	(Ca _{10.13} Mg _{0.01} Mn _{0.02})	(PO ₄) _{6.00} (OH _{1.50} F _{0.46} Cl _{0.02})	10.16	0.35
3. Switzerland	(Ca _{9.99} Mn _{0.01})	(PO ₄) _{6.00} (OH _{1.94} F _{0.54})	10.00	-0.48
4. Italy	(Ca _{10.10} Mg _{0.07})	(PO ₄) _{6.00} (OH _{0.03} Cl _{0.03})	10.17	2.18
5. France (Damour)	Ca _{9.94}	(PO ₄) _{6.00} (F _{1.88})	9.94	0.00
6. Theoretical	Ca _{10.00}	(PO ₄) _{6.00} (OH _{2.00})	10.00	0.00

Spectroscopic determination of copper in four synthetic samples of hydroxylapatite showed a correlation between intensity of pink color and adventitious copper. The pink color was easily observable in a sample containing about 0.003% Cu.

Dissociation of hydroxylapatite

Several years ago an attempt was made in the laboratory of the Bureau of Plant Industry²⁰ to measure the dissociation pressure of natural and synthetic hydroxylapatite. The experiments were not successful owing to the apparent irreversible character of the dissociation. It was found that this dissociation took place over an interval ranging from 1200°C. to 1500°C. These experiments also showed that if hydroxylapatite were heated so as to drive off almost one half of its water, the x-ray pattern of hydroxylapatite still persisted. However, if all the water were removed, a mixture of α -tricalcium phosphate and hilgenstockite (tetracalcium phosphate) resulted.

Another approach to this problem was made by Jacob, Reynolds, and Hendricks²¹ who studied the "citrate solubility" of hydroxylapatite as a function of the heat treatment of the charge. They heated synthetic hydroxylapatite to various temperatures and determined the solubility of the phosphate in neutral ammonium citrate, according to the official method for available phosphate. It was found that at temperatures below

²⁰ Nelson, R. A. Unpublished data, 1936.

²¹ Jacob, K. D., Reynolds, D. S., and Hendricks, S. B. Unpublished data, 1936.

1200°C. the "citrate solubility" remained the same; at temperatures between 1200°C. and 1500°C. it was greatly increased; and that above 1500°C. it was the same as a mixture of α -tricalcium phosphate and hilgenstockite. These studies were in agreement with the accompanying x-ray investigations made on the same materials and with observations of Trömel.¹³

PETROLOGY

Microscopic examination

In thin section the Swiss apatite consists of subhedral and euhedral crystals in a coarsely foliated talc in which the foliae are more or less



FIG. 4. Apatite-talc schist, Kemmleiten, Hospenthal, Kt. Uri, Surtzerl, Switzerland, ap=apatite, t=talc, solid black areas=magnetite.

FIG. 5. Hydroxylapatite-talc schist from the old verde antique serpentine quarry near Holly Springs, Cherokee County, Georgia. ap=apatite (hydroxylapatite), t=talc.

arranged in a parallel manner, with only occasional local areas exhibiting a decussate structure. The apatite has been invaded by talc crystals which occur as gash-like inclusions and narrow veinlets in the apatite. These talc areas usually behave as a unit. Tiny veinlets and irregular areas of carbonate were observed in some of the fluor-hydroxylapatite crystals. Excellently crystallized magnetite is scattered throughout the talc (see Fig. 4). The rock is an apatite-talc schist. A small portion of the associated steatite shows talc, magnetite, and chlorite. This chlorite is quite pleochroic, being pale emerald-green parallel to the cleavage and very pale yellow perpendicular thereto. The interference colors are anomalous, being a greenish-gray. The paragenetic sequence in the talc-schist is fluor-hydroxylapatite, talc, and magnetite.

The texture of the Georgia hydroxylapatite-talc schist is coarse. Long foliae of talc traverse the thin section and these are only rarely disturbed by small patches of talc cutting transversely across their length. Hydroxylapatite is subhedral and carries only long crystals of talc which are present as inclusions or as invading gash-like veinlets. These are to be seen in the camera lucida drawings in Fig. 5. The paragenetic sequence is hydroxylapatite, and talc.

Genesis

These talc schists, as judged by their accessory minerals (hydroxylapatite and magnetite), and the coarseness of the talc flakes, indicate metamorphism embodying hydrothermal reactions under dynamic stresses. They have arisen through the metamorphism of ultrabasic rocks. At the time of metamorphism a considerable amount of water was present to permit the formation of talc and hydroxylapatite. A definite upper temperature limit is set by the fact that at one atmosphere pressure talc dissociates into enstatite, a silica rich liquid, and water vapor between 800° and 840°C.²² As was pointed out earlier, hydroxylapatite dissociates at a still higher temperature, namely, 1200° to 1500°C. The effect of non-uniform pressure would probably lower these dissociation temperatures significantly and thus set the upper limit of formation of these rocks at correspondingly lower temperatures.

Both of the hydroxylapatites carry some fluorine. Accordingly, talc of these rocks and a totally unrelated pure talc were analyzed for their fluorine content in order to ascertain whether there was any competition between the talc and hydroxylapatite for the available fluorine. The results of the analyses are given in Table 5. The talc used as reference was from Harford County, Maryland, U.S.N.M. #82519, and consists of clear transparent books about 7 cm. in diameter.

TABLE 5. FLUORINE CONTENT OF MINERALS OF THE HYDROXYLAPATITE-TALC SCHISTS

Locality	%F in Talc (Mineral)*	%F in Hydroxylapatite
Georgia	0.009	0.16%
Swiss	0.008	1.01%
Maryland	0.006	no associated apatite

* Optically the Georgia and Swiss talcs were similar in that 2V seems smaller than the value observed for the Maryland talc. Precise measurement of 2V on the scrapings of the talcs prepared for analysis was not possible.

²² Ewell, H. H., Bunting, E. N., and Geller, R. F., Thermal decomposition of talc: *Jour. Res. Natl. Bur. Sids.*, **15**, 551-556 (1935).

The manner of formation of hydroxylapatite can partially be inferred from the observations discussed above. Minerals of the apatite group generally contain fluorine, even when formed in aqueous systems low in fluorine, such as the sea. Chlorine or hydroxyl are substituted for fluorine only under very unusual conditions, the former in some pegmatites and the latter in the presence of hydrous metamorphic minerals.

The parent rocks which gave rise to the talc schists were of an ultra basic character and contained small, but unusually important quantities, of phosphatic compounds. During the period of metamorphism a continuous and significantly large quantity of water was probably present, since the principal mineral, talc, requires 4.8% H_2O as hydroxyl groups. Hence, in the absence of sufficient fluorine to combine with the available phosphate, or in the presence of water at high temperatures, hydroxyl, supplied by the water, was taken from the system and hydroxylapatite resulted. Analyses of the talc, as listed in Table 5, gave no experimental evidence of competition for the fluorine content of the system. Nevertheless, the talc, because of its far greater bulk, may have removed sufficient fluorine to prevent the re-formation of fluorapatite, if it had existed as such before reorganization set in. As was pointed out in the comments on the determination of the water content of apatites, the passage of heated water vapor over fluorapatite removes important quantities of fluorine for which the hydroxyl is substituted. This process, carried out over a long period of time, would reduce the fluorine content of a fluorapatite very decidedly. The operation of this process might lead to some variability in the fluorine content of unrelated masses of the hydroxylapatite, and some evidence of this fact was noted. The assemblage of minerals—talc, hydroxylapatite, and magnetite—and the coarse foliation of the talc indicate dynamothermal metamorphism. Temperature and non-uniform pressure were both critical factors in the formation of these talc schists. The system was undoubtedly closed, permitting the development or maintenance of a pressure suitable for the formation of hydroxylapatite.

The Italian hydroxylapatite is reported to occur in a diallage-serpentine rock mass. Other associates include rose-colored sphene, magnetite, fibrous hornblende, chlorite, and ilmenite. Although the exact field relations of this rock mass are not fully described, it is suggestive of the serpentine masses commonly associated with talc schists. Further field observation would be of interest to ascertain whether the apatite is associated with serpentine or talc.

The associated fluor-hydroxylapatite-chlorite schists

The talc deposits are related to the associated chlorite schists. Speci-

mens of the chlorite schists examined consist principally of chlorite and fluor-hydroxylapatite, with talc in a few instances. The ω index of refraction was measured on the apatite of five different specimens and the value of each was found to be 1.645, which is significantly lower than ω of hydroxylapatite. Analyses of one sample, No. 2 in Table 3, showed the presence of 0.84% F and 0.06% Cl. This apatite occurs as masses resembling very oblate spheroids, as large as 5 cm. in diameter, which are embedded in a medium-grained chlorite schist. The measurements on the chlorite of the chlorite schist are given in Table 6.

TABLE 6. DATA ON THE CHLORITE FROM THE OLD VERDE ANTIQUE QUARRY
NEAR HOLLY SPRINGS, CHEROKEE COUNTY, GEORGIA

Chemical Data	Spectroscopic Data	Optical Data
P ₂ O ₅ =0.08	Major Constituents: Mg, Al, Si, Fe	Biaxial (+) 2V=15°±
F=0.007		
H ₂ O at 100°C.=none		$r < v$
H ₂ O at 600°C.=3.10%	Very Minor: Mn, K, Na, P	$\alpha = 1.586 \pm 0.002$ $\gamma = 1.595 \pm 0.002$
H ₂ O at 1000°C.=11.46%		
H ₂ O at 1200°C.=12.18%		$\gamma - \alpha = 0.009$
H ₂ O at 1400°C.=12.58% fused	Sought, but not found: Li, Ca, Sr	

It is known from the researches of Doelter,²³ and Doelter and Dittler,²⁴ that chlorite dissociates to yield water vapor, glass and various crystalline phases. J. Orcel²⁵ found that a strong exothermic reaction, corresponding to the major loss of water, takes place in the range of 600°C.–800°C. for most of the chlorites that he examined. Analyses, Table 6, show that the chlorite studied in this work loses most of its water below 1000°C.

Chlorite resembles talc in being a very hydrous mineral, formed extensively by metamorphism in the presence of abundant water. Association of hydroxylapatite, or fluor-hydroxylapatite, with chlorite schists is thus similar to the association of these minerals with talc schists. From physicochemical considerations, the environment at the time of the metamorphism which produced the talc schists and the chlorite schists was nearly the same and permitted the contemporaneous development of

²³ Doelter, C., *Synthetische Studien: Neues Jahrb. Min.* **1**, 3 (1897).

²⁴ Doelter, C., and Dittler, E., *Über einige Mineralsynthesen: Sitzber. Akad. Wiss. Wien*, **121**, 899–914, 1910 (1912).

²⁵ Orcel, J., *L'analyse thermique des chloritès: Compt. rend.*, **183**, 565–567 (1926).

both rocks. This agrees satisfactorily with the field evidence on the intimate association of talc and chlorite schists.

DESCRIPTION OF THE GEORGIA OCCURRENCE OF HYDROXYLAPATITE

The Georgia occurrence of hydroxylapatite crystals is in the serpentine quarry located about two miles southwest of Holly Springs in Cherokee County, about five miles north of the Cobb County line. The quarry is on a hill side in a rough, broken region near the head of one of the tributaries of Blanket Creek. McCallie²⁶ described the deposit and the early workings for talc and verde antique. He also described some of the structural and physical characteristics of the serpentine.

The area about the quarry is hilly country representing the foothills of the Appalachian Mountains. The country rock of this region and of all the piedmont and mountain regions of Georgia is of ancient origin, generally presumed to be pre-Cambrian or early paleozoic in age. There are very few recognizable sediments and most rocks of the crystalline area are igneous or metamorphic. The rocks comprising the largest distinguished group in this area of Georgia are those of the Carolina series, which vary from a hard biotite gneiss to mica schists, often cut by pegmatite dikes. A particular facies of the Carolina series is known as the Ashland schist. The serpentine quarry near Holly Springs is in a lenticular body of ultrabasic rock apparently intruded into the biotite gneiss and Ashland schist. The ultrabasic body is approximately 150 feet wide at the widest portion near the center and is approximately 600 feet long. The strike of the schistosity varies from N. 25° E. to N. 35° E., and averages around N. 30° E. The dip is 83 degrees to the southeast, although folding makes this value somewhat uncertain. Approximately five miles further southwest along the line of strike a similar body is said to outcrop.²⁷

The ultrabasic rock-body now consists mainly of hard serpentine and dark green chlorite schist, both cut by veins of foliated talc of a light sea-green color. In places the talc is bordered by crusts of magnesite of an iron-bearing variety known as breunnerite.²⁸ It is probably to be assumed that the mass was intruded as a peridotite and has changed in place to serpentine, chlorite, talc, and magnesite. There has been considerable metamorphism as the talc varies in character from the beautiful green

²⁶ McCallie, S. W., *The marbles of Georgia*, 2nd ed.: *Geol. Survey Ga., Bull.* 1, 114-116 (1907).

²⁷ Crickmay, G. W., *The geology of the crystalline rocks, geologic map of Georgia: Georgia Division of Mines, Mining, and Geology*, Atlanta (1939).

²⁸ Foshag, W. F. Personal communication to F. A. Daniel, December 13, 1939.

micaceous, or foliated variety, to twisted radially crystallized masses of lighter color, and in still other places to a dull gray mass filled with small crystals of magnetite and chromite. In some places magnetite crystals were noted which had been flattened by gliding of one face on the other. Some hardened talc was also noted, and this variety seemed to have a surface quite suggestive of slickensides. The apatite occurs in the micaceous talc, magnetite filled talc, and in the dark green chlorite schist. A crystal was noted which was formed squarely across the boundary of talc and chlorite. The apatite crystals are normally of a lemon yellow color, and usually of poorly developed crystal form, but some specimens were found having an apple-green color.

There are places in the quarry where thin layers of chlorite alternate with thin layers of talc, with the layers twisted and distorted by much local folding. Such a mass of interlayered talc and chlorite grades into serpentine of a hard, dark green variety. In some spots, the serpentine has a purplish cast. Surfaces were found where asbestiform serpentine had been developed.

Most ultrabasic rocks in the Georgia crystalline area, other than the trap dikes of Triassic age, are generally considered as part of the Roan gneiss, an ancient rock of somewhat doubtful age.²⁹ However, basic and dioritic rocks are fairly common over the crystalline area of Georgia. A dark green chlorite schist similar to that in the quarry is found as the country rock of the famous Little Bob pyrite mine, 25 miles southwest of the quarry. A basic injection into the pegmatite near Kennesaw Mountain, 15 miles south, has changed the feldspar there into a high-calcium plagioclase and has led to development of large hornblende crystals. Other instances of basic rocks in the vicinity are known, but a connection between them and the serpentine has not been established. No specimens of hydroxylapatite have been reported as found at other localities than in the quarry.

ACKNOWLEDGMENTS

W. L. Hill offered valuable suggestions during the course of the work and in the preparation of the manuscript. Dr. W. F. Foshag of the U. S. National Museum kindly supplied us with several specimens from the museum collections. We are indebted also to Dr. B. C. Brunstetter and A. T. Myers of the Bureau of Plant Industry for a number of spectroscopic analyses.

²⁹ Crickmay, G. W., Status of the Talledega series in southern Appalachian stratigraphy: *Bull. Geol. Soc. Am.*, **47**, 1371-1392 (1936).

CRYSTAL STRUCTURE OF GILLESPITE, $\text{BaFeSi}_4\text{O}_{10}$

A. PABST,

University of California, Berkeley, California.

ABSTRACT

Gillespite has been studied by means of rotation, oscillation, Laue and powder x -ray patterns. It belongs to the space group D_{4h}^8-P4/ncc . The unit cell, $a=7.495\pm0.010$ Å, $c=16.050\pm0.010$ Å, contains 4 $\text{BaFeSi}_4\text{O}_{10}$.

A structure with eleven parameters has been found which yields satisfactory agreement of calculated and observed intensities. It is a silicate sheet structure with oxygen atoms in three kinds of positions and unshared corners of SiO_4 tetrahedra on both sides of the sheets. Single and double fourier summations give an excellent check on the structure. Interatomic distances are of expected magnitude. Barium has an 8-fold coordination and iron a 4-fold coordination.

The leaching of gillespite is discussed.

INTRODUCTION

Gillespite was described as a new mineral by Schaller¹ from a "small rock specimen collected from a moraine . . . near the head of Dry Delta, Alaska Range, Alaska." At first the crystal system to which it belongs was not established but it was found to be "optically uniaxial." Upon later reexamination² Schaller described it as tetragonal because it showed poor rectangular cleavage in addition to the eminent basal cleavage. Other minerals identified in the specimen from which gillespite was described were celsian, hedenbergite and quartz.

Gillespite has been found in only one other locality,³ near Incline, Mariposa County, California. There it is found with the new mineral sanbornite, BaSi_2O_6 , celsian, witherite (?), diopside, tourmaline, quartz and pyrrhotite. No geologic study of the occurrence has been made, but it is stated to be "probably from a contact metamorphic zone."

The x -ray data for this study were obtained during 1938-39 while the writer held a fellowship of the John Simon Guggenheim Memorial Foundation. Most of the diffraction patterns were made in the Department of Mineralogy of the British Museum of Natural History, the facilities of which were graciously made available by Dr. W. Campbell Smith and Mr. F. A. Bannister. One important pattern was also obtained in the crystallographic laboratory of the University of Cambridge through the courtesy of Dr. A. J. Bradley and Mr. H. Lipson. Later phases of

¹ Schaller, W. T., Gillespite, a new mineral: *Jour. Wash. Acad. Sci.*, **12**, 7-8 (1922).

² Schaller, W. T., The properties and associated minerals of gillespite: *Am. Mineral.* **14**, 319-322 (1929).

³ Rogers, A. F., Sanbornite, a new barium silicate mineral from Mariposa County, California: *Am. Mineral.*, **17**, 161-172 (1932).

the work were aided by a grant from the Committee on Research of the University of California.

MATERIAL

Small fragments of nearly pure gillespite from the Alaska locality were kindly furnished by Dr. Schaller and Professor Rogers. Dr. A. A. Fitch gave some specimens of sanbornite from the California locality from which it was possible to separate a supply of clean fragments of gillespite. No difference whatever can be observed in the x -ray patterns of gillespite from the two localities.

CELL DIMENSIONS, CONTENT AND DENSITY

The cell dimensions were first determined from a powder pattern with Mo rays made by Mr. W. H. Dore of the Division of Plant Nutrition, University of California. This pattern showed no lines for which l is odd and hence led to a halved value of c . That the structure practically has a pseudo-cell with half the c dimension even resulted in the absence of odd layer lines on the first c axis rotation patterns. Finally these layer lines were detected on long exposure oscillation patterns and it was possible to observe a few lines with l odd on an excellent powder pattern with Co radiation.

The best determinations of cell dimensions were made from the two powder patterns mentioned after the indexing had been checked by other means.

It has long been customary among x -ray crystallographers to use the x -ray wave lengths based on Siegbahn's *assumed* grating space for calcite, $3.02904\text{\AA}$.⁴ If this is done one should also use a value of Avogadro's number, or for the mass of atom of unit atomic weight which is consistent with these wave-lengths. Siegbahn⁵ uses 60.594×10^{22} for Avogadro's number which he calls "Loschmidtsche Zahl." The reciprocal of this, 1.6503×10^{-24} grs., should be used as the mass of an atom of unit atomic weight together with the "Siegbahn" wave lengths. Unfortunately slightly different values have often been used.

Reconsideration of the general physical constants by various physicists has shown that the values used by Siegbahn have received notable correction by later work and that this largely reconciles the discrepancy which Siegbahn noted between his wave lengths and those obtained from line grating experiments. In a recent paper Donnay⁶ used the value,

⁴ See, for instance, *Handbook of Physics and Chemistry*, 23rd. ed. 1939, *International Tables for the Determination of Crystal Structures*, vol. II, (1935), etc.

⁵ Siegbahn, M., *Spektroskopie der Röntgenstrahlen*, p. 43 (1931).

⁶ Donnay, J. D. H., Morphologie cristalline du groupe de la schéelite: *Trans. Roy. Soc. Canada*, 36, 37-51 (1942).

60.23×10^{22} , for Avogadro's number, which he obtained from the results of Dunnington, to calculate the cell dimensions of members of the scheelite group from observed densities and goniometric constants. He compared the results of his calculations with cell dimensions for these minerals, determined in 1927 or earlier, with the use of Siegbahn wave lengths based on a different value of Avogadro's number. This procedure does not lead to comparable results.

TABLE 1. CELL DIMENSIONS AND DENSITY OF GILLESPIITE

	Mass of atom of unit atomic weight	Unresolved K_{α} radiation		<i>a</i>	<i>c</i>	Density calc.
		λ_s	λ_b			
Berkeley Film Mo radiation cassette radius 203.2 mm.	1.6503×10^{-24} g.	0.7100	—	7.499	16.054	3.403
	1.66035×10^{-24} g.	—	0.7114	7.514	16.086	3.403
Cambridge Film Co radiation cassette radius 190.6 mm.	1.6503×10^{-24} g.	1.7872	—	7.491	16.046	3.412
	1.66035×10^{-24} g.	—	1.7908	7.506	16.078	3.412
Average values, Siegbahn system				7.495 ± 0.010	16.050 ± 0.010	3.407

The best consistent values of the physical constants presently available are doubtless those given by Birge.⁷ In Table 1 are shown results of calculations for gillespite from two powder patterns. For each pattern the calculation is made in two ways, first using the customary Siegbahn wave lengths with the appropriate value of the mass of an atom of unit atomic weight, and then using the value for this constant given by Birge, together with wave lengths increased by the factor 1.002034, also given by Birge, to be consistent therewith. International Atomic Weights of 1939 were used. It may be noted that the ratio of the two values of the mass of an atom of unit atomic weight is just the cube of the ratio of the wave lengths and thus the calculated density is the same when consistent constants are used.

The calculated density is much higher than that reported by Schaller, 3.33, but agrees well with three determinations on clean fragments from California, 3.399, 3.404 and 3.402, average 3.402, with the Berman bal-

⁷ Birge, R. T., A new table of values of the general physical constants: *Reviews of Modern Physics*, **13**, 233-239 (1941), and The general physical constants: *Reports of Progress in Physics*, **8**, 90-138 (1942).

ance. Two fragments from Alaska, furnished by Schaller, gave 3.390. All of my observed and calculated values lie within the range 3.40 ± 0.02 , corresponding to a cell content of 4 $\text{BaFeSi}_4\text{O}_{10}$. In view of the numerous checks it seems that both the Alaska and the California gillespite show no significant departure from Schaller's formula.

TABLE 2. SUMMARY OF OSCILLATION PATTERNS OF GILLESPIITE, c AXIS, CO RAYS

hk $\downarrow$	$l \rightarrow$	0	1	2	3	4	5	6
10				—		S		—
11	M*			S		VS		VS
20	VW			VS		VS		M
21			VW	M	—	—	—	W
22	S			M		M		M
30				W		VW		—
31	M		VW	S	—	S	VW	S
32			VW	VW	—	M	—	—
40	VS			M		VW		S
41			W	—	—	W	VW	—
33	—			W		S		M
42	M		—	S	—	W	—	VW
50				—		M		—
43			W	W	—	—	VW	—
51	W		—	M	W	S	—	M
52			VW	M	—	—		VW
44	M			W		W		W
53	M		—	M	VW	M	—	M
60	M			S		M		VW
61			—	W	VW	—	—	—
62	M		—	M	—	M	—	W
54			W	VW	—	VW	VW	—
63			—	—	—	VW	—	—
70				W		—		—
71	M		—	M	W	M	—	S
55	W			M		—		—
64	S		—	M	—	W	—	M
72			VW	—	—	W		—
73	VW		VW	S	W	S		—
65			—	M				—
80	M			M				—
81			—	—				—
74			W	W				—
82	VS							—

* From powder pattern.

Dashes indicate that "reflections" permitted in space group $P4/ncc$ were not observed. Vacant spaces correspond to the extinctions required by space group $P4/ncc$.

SPACE GROUP

Laue patterns indicate the Laue group $4/mmm$. Table 2 shows a tabulation of all lines observed on c axis rotation and oscillation patterns. Appearance of $hk0$ with $h+k$ even only shows that 001 is an n plane and the appearance of hhl and $h0l$ with l even only shows that 110 and 100 are c planes. This indicates the space group $D_{4h}^8 - P4/ncc$. Due to the n glide plane, odd layer lines of [110] rotation patterns are almost unoccupied and due to the c glide planes and absence of heavy atoms in general positions, the odd layers of [001] rotation patterns are very weak (Table 2).

DETERMINATION OF THE STRUCTURE

It is necessary to distribute 4 Ba, 4 Fe, 16 Si and 40 O among the positions:

4-fold	8-fold	16-fold
(a) $00\frac{1}{2}$ etc.	(d) $\frac{1}{4}\frac{1}{4}0$ etc.	(g) xyz etc.
(b) 000 etc.	(e) $00z$ etc.	
(c) $0\frac{1}{2}z$ etc.	(f) $xx\frac{1}{2}$ etc.	

A rough estimate of the x 's and y 's can easily be obtained from the observed intensities of the first few $hk0$ lines. It is unlikely that ions of such different radii as Fe and Ba should share a set of positions and the possibility of partially filled positions is set aside unless later considerations require that it be taken into account. With any distributions of Ba and Fe in the 4-fold positions these atoms give a maximum contribution to the 200 "reflection." Since this line is very weak, or absent, it follows that most of the lighter atoms must be clustered about a position with coordinates x, y somewhere near $\frac{1}{4}, \frac{1}{4}$. If these light atoms are so situated, 110 will be strong if both Fe and Ba are in positions (a) and (b), or if both are in positions (c), whereas the intensity of 110 would be weak to moderate if one of the heavy atoms is in (a) or (b) and the other in (c). Since 110 is observed as a weak line it seems that Ba is in (a) or (b) and Fe in (c), or vice versa, the choice between these possibilities being made after a more extended check of intensities.

From the fact that the ratio of Si to O is 2/5 and that gillespite has an excellent basal cleavage it seems certain that it has a silicate sheet structure. How such a structure may be reconciled with the requirements just outlined is shown in Fig. 1, in which SiO_4 tetrahedra are shown as triangles. In Fig. 1, A, B and C, each corner of an equilateral triangle corresponds to an oxygen atom and there is another oxygen atom above or below the center of each such triangle. Figure 1A shows the common hexagonal or pseudo-hexagonal Si_4O_{10} sheet found in micas and related minerals. It is also possible to make a tetragonal Si_4O_{10} sheet like that in

Fig. 1B. If the square groups of four SiO_4 tetrahedra are overlapped as in Fig. 1C, the tetrahedra in full lines pointing downward and those in broken lines pointing upward, form a continuous sheet of tetrahedra at

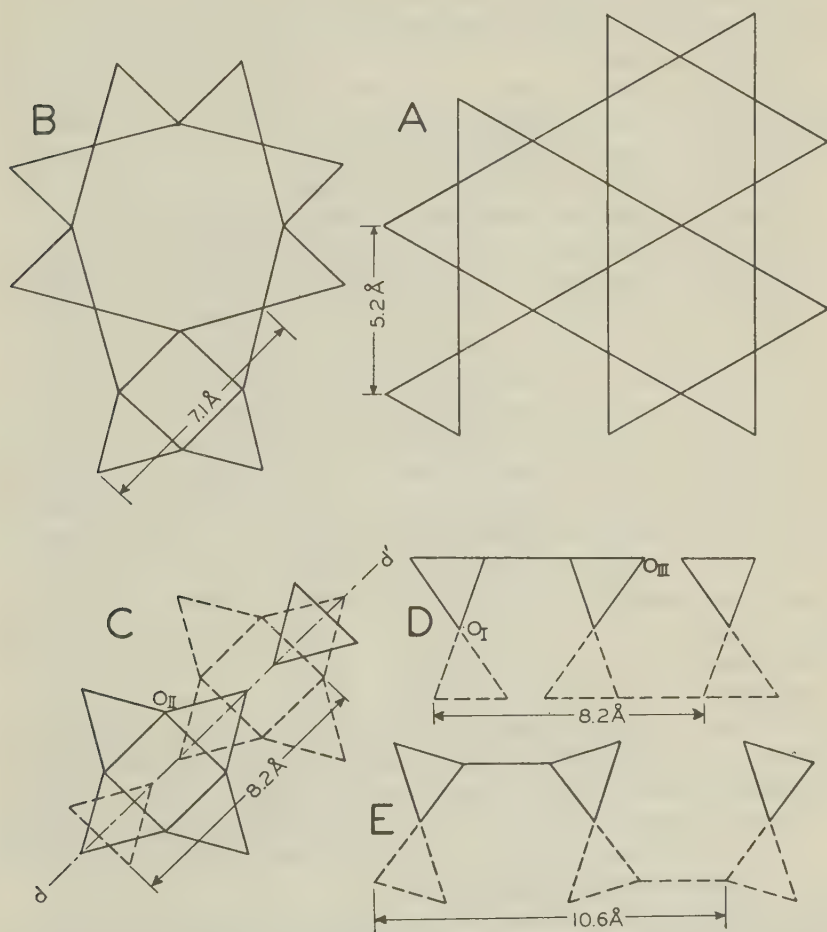


FIG. 1. Linking of SiO_4 tetrahedra to form Si_8O_{20} sheet.

two different levels, as shown in Fig. 1D which is a section through Fig. 1C along the line $d-d'$. In such a sheet the oxygens are of three different sorts, O_{III} at unshared corners, O_{II} (indicated in Fig. 1C) at corners shared by two tetrahedra at the same level, and O_{I} (indicated in Fig. 1D) at corners shared by two tetrahedra at different levels. There are, of course, an equal number of O_{III} 's and O_{II} 's and half as many O_{I} 's.

The squares of Fig. 1C may be fitted about the 4-fold axes in position (c) leaving the overlapped tetrahedra clustered about $(x, y) = (\frac{1}{4}, \frac{1}{4})$.

The dimensions given in the several parts of Fig. 1 all depend on the assumption that the length of an SiO_4 tetrahedron edge is close to $2.6\text{\AA}$. The distance $5.2\text{\AA}$ of Fig. 1A corresponds to the common a axis spacing of micaceous minerals. It will be seen that adjacent unshared corners, O_{III} , in Figs. 1C and 1D are much closer together than is compatible with the known oxygen radius. This can be corrected by canting the tetrahedra and expanding the sheet as shown in Fig. 1E. In this figure the operation has been carried just far enough so that the identity distance along $[110]$ becomes $10.6\text{\AA}$, which is the value for gillespite.

The vertical dimension of such a sheet as that just described would be a little under $8\text{\AA}$ and there would be 8 Si in a sheet within the cell limits. It follows that there are two sheets in a cell and O_I must be in position (d) $\frac{1}{4}\frac{1}{4}0$ or in (f) $xx\frac{1}{4}$, with x nearly equal to $\frac{1}{4}$, to correspond to the description just given. Assuming no deformation of tetrahedra it is possible to derive x and y coordinates for all atoms. Calculated intensities from such a structure give only a rough agreement of $hk0$ intensities, showing that a further shifting of the sheet is required. This is easily accomplished with O_I in (f) $xx\frac{1}{4}$ by assigning to x some value other than $\frac{1}{4}$. The section shown in Fig. 1E then no longer lies in one plane but is offset as shown in the final picture of the structure, Fig. 4. Various values of x for O_I were tried in the range 0.20 to 0.25 with appropriate values of x and y for other atoms and the parameters given in Table 3 selected from intensity comparisons.

All intensity calculations were made with f values for Si^{+4} , O^{-2} , Fe and Ba taken from the International Tables for the Determination of Crystal Structures. Suitable plane frequency and glancing angle factors for rotation or powder patterns were used and no other corrections made.

Visual estimates of intensities were checked by photometer curves on the Co powder pattern and the zero layer lines of $[uv0]$, $[120]$, $[110]$, $[100]$ and $[001]$ Co rotation patterns.

Table 3 shows that Ba must lie in position (a) or (b) whereas Fe is in position (c). The last column shows that there is no agreement of intensities if these two are interchanged. Patterns with Co radiation were chiefly used in all intensity comparisons to avoid the high absorption of Fe in gillespite for Cu radiation. In Table 3 a few observed and calculated intensities are also given for Cu radiation because they extend the range of agreement beyond the limit observable with Co rays and in this range of high glancing angles the effect of absorption is less serious. The only noteworthy discrepancies are the relative weakness of the ob-

served intensities for 110 and 220 compared to calculated intensities. This is presumably due to absorption and/or extinction which may

TABLE 3. OBSERVED AND CALCULATED INTENSITIES OF $hk0$ LINES OF GILLESPIITE

Observed Intensities#					Calculated intensities					
					x		y			
					Si	0.27	0.175	O _{II}	0.465	0.240
					O _I	0.215	0.215	O _{III}	0.135	0.275
					Ba in 0, 0		Ba in 0, 1/2			
					Fe in 0, 1/2		Fe in 0, 0			
Pattern	[010]	[110]	[001]							
Radiation	Co	Co	Co	Cu	Co	Cu	Co			
$hk0$										
110		1	1		22.2				59.6	
200	—		—		5.4				5.4	
220		5	5		120.0				120.0	
310			4		37.8				10.6	
400	4		10		91.5				91.5	
330		—	—		1.3				16.6	
420			4		62.8					
510			1		2.3					
440		2—	2		13.3					
530			3		15.5					
600	2—		3		15.8					
620			3		17.7					
710			3—	}*	13.5					
550		—	1		2.4					
640			5		72.4					
730			—		4.4					
800	2—		4		43.8					
820			6	6	151.0	41.9				
660				—		4.9				
750				1		6.2				
840				2		31.0				

* These two lines are superposed in [001] rotation patterns. The observed intensities given for them are from oscillation patterns. All other observed intensities are from rotation patterns.

Scale of intensities; 1—very weak, 10—very strong.

make itself felt for the first few lines even on patterns with Co rays and to the difficulty of accurate observation of intensities for rays scattered from the edges of a thin flake. A check is obtained by comparison of the

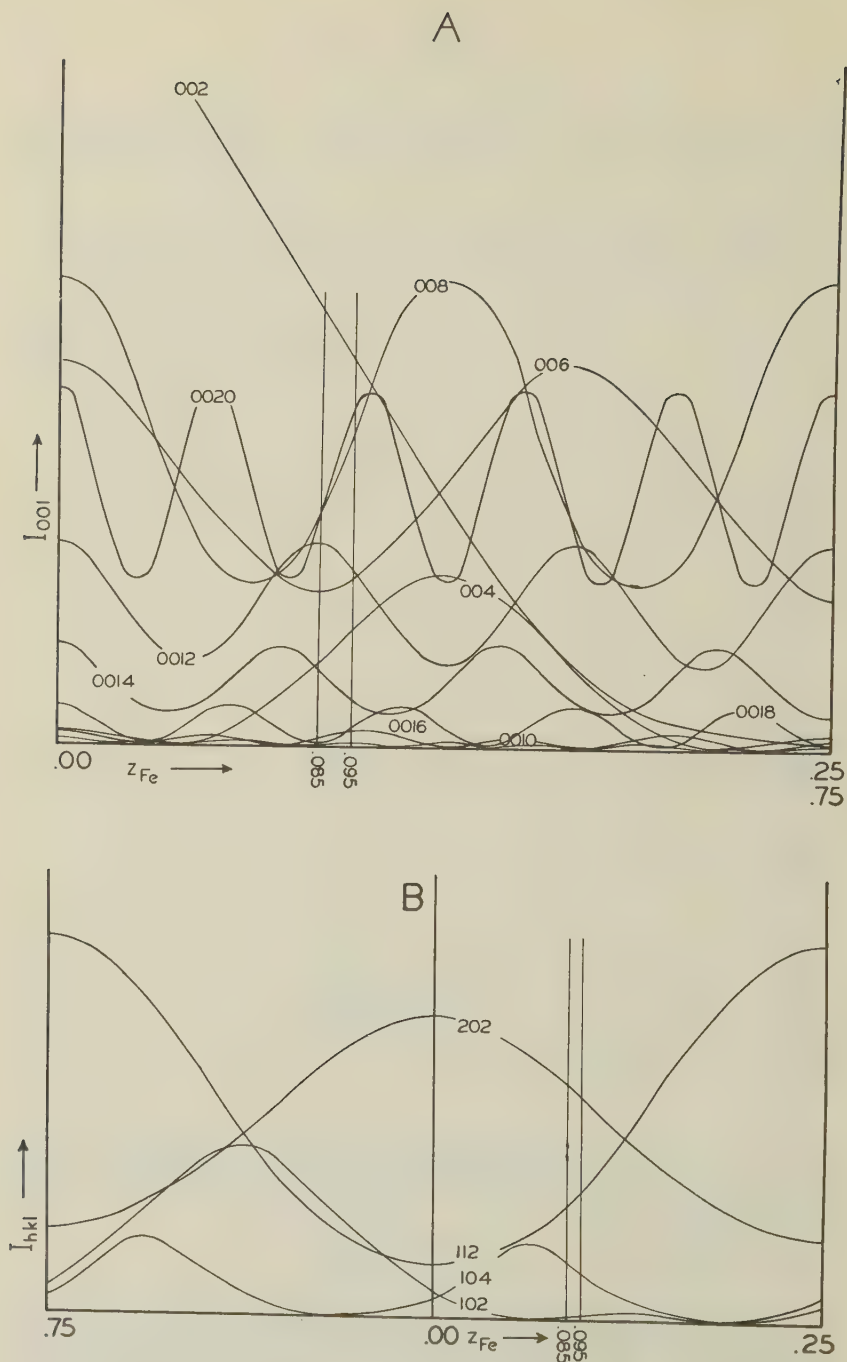


FIG. 2. A. Variation of $00l$ intensities with z_{Fe} when z parameters for other atoms are: Ba 0, Si .155, O_I $\frac{1}{4}$, O_{II} .14, O_{III} .095. Only even orders allowed by space group. Compare observed intensities (Cu) in Table 4.

B. Variation of intensities for a few pyramid planes with z_{Fe} . z for other atoms as in A. Compare observed intensities in text.

several orders of $h00$ and of $hh0$ on $[010]$ and $[1\bar{1}0]$ rotation patterns also shown in Table 3.

Accepting the values of x and y thus determined one can calculate the z for Si, O_{II} and O_{III} on the continued assumption that SiO₄ tetrahedra are essentially undistorted. This gives the following: $z_{\text{Si}} = .155$, $z_{\text{OII}} = .14$ and $z_{\text{OIII}} = .095$.

It is now possible to select a parameter for Fe and to choose between positions (a) and (b) for Ba by consideration of intensities of $00l$. A likely position for Fe would seem to be in $0, \frac{1}{2}, .095$, where it would lie in a square of O_{III}'s at a distance of $1.97\text{\AA}$ from each.

The observed intensity of $006 < 0012 < 008$. From Fig. 2A it may be seen that a z_{Fe} parameter near the range .085 to .095 is in agreement with this. A discrepancy remains in the slightly low observed intensity of 002, which appears weaker than 008, but this may again be ascribed to absorption and/or extinction.

Figure 2A gives $00l$ intensities for Ba in (b) 000. If Ba is in (a) $00\frac{1}{4}$, the calculated intensity of 0010 is high for any value of z_{Fe} . Since 0010 is not observed, this determines the choice of the position (b) 000 for Ba.

This still leaves z_{Fe} undetermined because all orders of $00l$ will show the same intensity with Fe in z or in $\bar{z}$, but in .905 or .915 Fe would be in quite a different position in the structure than in .095 or .085, remote from any O to which it may reasonably be expected to be tied. Fortunately it is easy to choose between these alternatives by considering only a few other lines. On a Co powder pattern the observed intensities of the first few lines due to pyramid planes are:—

102	112	104	202
absent	strong	medium	very strong.

Figure 2B shows clearly that the z parameter first selected for Fe yields excellent agreement and that the corresponding value $\bar{z}$ is not compatible with intensities.

It will be seen that in Fig. 2A the agreement of the intensities (compare Table 4) is slightly better when Fe is near .085 than when it is in .095, just within the square of O_{III}'s where one might expect it. The parameter .095 for O_{III} was calculated from the x and y parameters of the structure on the assumption that the SiO₄ tetrahedra are virtually undeformed. Actually small deformations have generally been found in well determined silicate structures. Nearly the same change in intensities of $00l$ as by shifting Fe from $z = .095$ to $z = .085$ can be obtained by shifting both Fe and O_{III} to $z = .09$. This results in only a trifling distortion of the SiO₄ tetrahedra and leaves the Fe just within the oxygen square. Intensity calculations for many lines were carried out for all

three of these cases. Agreement is as good or better when Fe and O_{III} are both at $z = .09$ and so this was chosen for the final set of parameters:

		x	y	z		x	y	z
4	Ba (b)	0	0	0	8	O _I (f)	.215	.215 $\frac{1}{4}$
4	Fe (c)	0	$\frac{1}{2}$	.09	16	O _{II} (g)	.465	.24 .14
16	Si (g)	.27	.175	.155	16	O _{III} (g)	.135	.275 .09

Tables 4 and 5 show the calculated intensities corresponding to these parameters and the observed intensities on various films. Agreement is satisfactory throughout.

TABLE 4. OBSERVED AND CALCULATED INTENSITIES OF SPOTS ON SOME ROTATION PATTERNS OF GILLESPIE

00 <i>l</i>						<i>h</i> 0 <i>l</i>		
Observed				Calculated		Observed	Calculated	
Rotation axis	[<i>uv</i> 0]	[110]	[120]				[010]	
Radiation	Cu	Co	Co	Cu	Co		Co	Co
002	5	.6	5	68.2	60.5	102	—	1.8
004	4	5	5	10.7	9.1	104	5	43.5
006	6	7	7	19.3	15.9	202	6	155.0
008	10	10	10	30.6	24.6	204	5	60.4
0010	—	—	—	0.9	0.7	106	—	1.0
0112	8	8	8	26.5	24.4	302	1	7.6
0014	5	4	5	10.5	11.2	206	1—	5.6
0016	—	—	—	0.3	0.5	304	—	1.5
0018	—			0.3		108	4	18.3
0020	6			32.9		306	} 2#	0.6#
						402		14.6#
						208	1	9.6
						404	—	2.7

Coincidence, compare table 2, where 306 is absent and 402 medium.

FOURIER ANALYSES

The structure of gillespite may be conveniently checked by fourier analyses. A one-dimensional summation can be made which gives the electron density projected upon the c axis,

$$\rho_z \sim \sum_0^l F_{00l} \cos 2\pi lz.$$

TABLE 5. OBSERVED AND CALCULATED INTENSITIES FOR A PATTERN OF GILLESPIE WITH CO RADIATION

<i>hkl</i>	Height of photometer curve peak	Calculated intensity	<i>hkl</i>	Height of photometer curve peak	Calculated intensity
002	6.0 mm.	1,086	322	2.5 mm.	145 { 34 111
102	—	45	008		
110	2.5	263	323	2.0	168 { 13 155
112	8.5	1,334	108		
004	2.5	117	315	—	21
200	—	41	217	—	2
104	4.5	678	226	—	61
202	14.0	2,329	118	5.0	580 { 196 384
211	4.0	200	400		
114	11.5	1,466	324	1.0	172
212	4.5	385	306	0.5	124 { 5 119
213	—	9	402		
204	6.5	713	411	—	60
006	6.0	822 { 93 729	316	4.5	620 { 614 6
220			412		
214	0.5	63	208	—	77
106	2.5	365 { 12 353	330	—	5
222			325	—	6
116	8.0	987 { 700 82	332	0.5	83 { 82 1
302			413		
310	—	205	218	—	0
311	—	27	404	—	21
215	—	0	420	1.0	236
312	3.5	452	421	—	1
224	2.5	259	414	—	68
206	1.5	58 { 54 4	317	—	0
313			326	2.5	424 { 1 423
304	—	15	422		
216	1.0	54	334	1.5	265
321	1.0	65	0010	—	2
314	4.5	482			

The *F* values were taken to be

$$\sqrt[2]{\frac{I_{\text{obs}}}{1 + \cos^2 \theta \sin 2\theta}}$$

without further correction. Only one quarter of the cell height need be calculated since the projection of the structure onto the *c* axis is symmet-

rical at 0, $\frac{1}{4}$, $\frac{1}{2}$, etc. The Lipson and Beevers strips can be used to great advantage in this case. If the l 's of all observed $00l$'s are halved (only even l allowed by space group) and results plotted for a pseudocell of $c/2$, points are obtained at each $1/120$ of the true cell height instead of the usual $1/60$ when these strips are used. By calculating a few additional points near $z = .09$ and $z = .15$ a very satisfactory projection of the electron density onto the c axis, almost a side view of the structure, is quickly obtainable. The result is shown on the left side of Fig. 3. The peaks corresponding to Ba, Fe and 4 O_{III} , 4 O_{II} and 4 Si, and to 4 O_I appear at the levels of the z parameters previously chosen. These peaks also are of such sizes as correspond closely to the numbers of scattering electrons situated at the several levels.

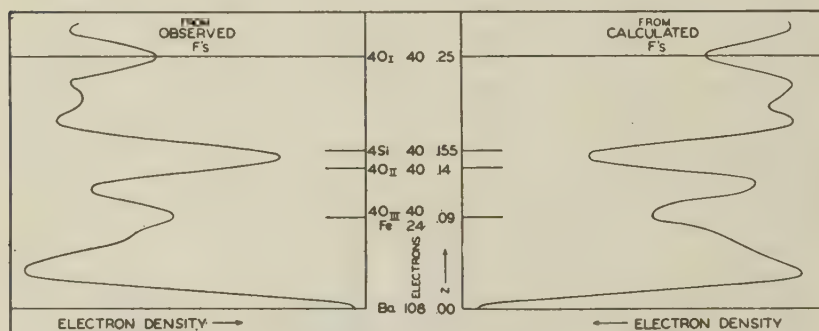


FIG. 3. Electron density as a function of z for one quarter of the cell height of gillespite from fourier summations of observed and of calculated F 's.

There is a small peak near $z = .21$. It can be seen that this is spurious and not due to any other scattering matter at this level by comparing with the ideal curve shown on the right of Fig. 3 which shows a similar peak near this level. This is due simply to the limited number of orders available for the summation.

Since the basal projection of the gillespite structure has a center of symmetry it is feasible to make a fourier summation for it from observed intensities of $hk0$ lines. For this it is necessary to make summations over only $1/16$ of the area, but it was found convenient, again using the Lipson and Beevers method, to make summations for $\frac{1}{8}$ of the area, $\frac{1}{2}a \times \frac{1}{4}a$, affording a complete check of the result.

The contoured fourier diagram is shown in the upper left quadrant of Fig. 4. The details of the silicate sheet are somewhat obscured by the

superposition of many atoms in the projection, as shown in the upper right quadrant.

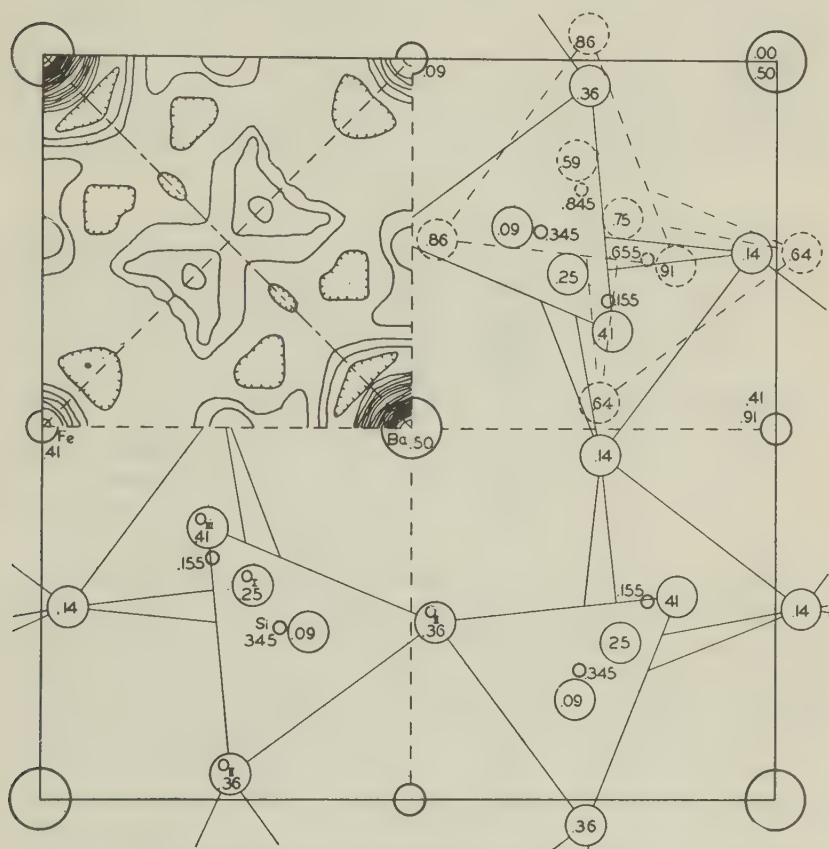


FIG. 4. Structure of gillespite projected onto 001. Lower half of diagram shows only one Si_8O_{20} sheet. In the upper right the other sheet is shown by broken lines. Upper left is electron density diagram obtained by fourier summation.

DISCUSSION OF THE STRUCTURE

In the lower part of Fig. 4 only one of the silicate sheets in the cell is shown in order to bring out the linkage. In the lower left quadrant the labelled Si is at the center of the tetrahedron with labelled O's at the corners. The labelled Fe and Ba are those closest the O_{III} corner of this tetrahedron. Other atoms are identified merely by their z coordinates and circles of appropriate sizes.

The entire upper Si_8O_{20} sheet is derivable from the lower sheet by glide reflection on the n plane in $xy0$ or $xy\frac{1}{2}$. This operation can be seen in the diagram by the glide reflection of the tetrahedra shown in full lines in the lower left to the positions shown in dashed lines in the upper right quadrant.

Both Ba and Fe lie between the sheets, but each Fe is at a minimum distance or bound to the O_{III} 's of only one sheet, whereas Ba is at a minimum distance or bound to O_{III} 's in both the upper and lower sheets, as the following tabulation shows:

	x	y	z	
Labelled Fe in Fig. 4	$\frac{1}{2}$	0	.41	
nearest	.635	.225	.41	lower Si_8O_{20} sheet
O_{III} 's	.275	.135	.41	
	.365	.775	.41	
	.725	.865	.41	
Labelled Ba in Fig. 4	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	
nearest	.635	.225	.41	lower Si_8O_{20} sheet
O_{III} 's	.365	.135	.41	
	.775	.635	.59	upper Si_8O_{20} sheet.
	.225	.365	.59	

Each Si_8O_{20} sheet has four oxygens (O_{III}) bound to but one silicon on its upper side and four on its lower side within each cell. Each such oxygen is tied to one Ba and one Fe. Since all of the O_{III} 's tied to each Fe are in the same sheet it follows that each Fe belongs definitely to a particular sheet, whereas each Ba is tied to O's above and below. In this way successive sheets are held together by the larger positive ions and the smaller positive ions lie within a single sheet. To this extent the linkage of this structure resembles that of micas.

TABLE 6. INTERATOMIC DISTANCES IN GILLESPIE

Edges of SiO_4 tetrahedron	Si— O_{I} 1.59 Å
O_{I} — O_{III} 2.67 Å	Si— O_{II} { 1.56
O_{I} — O_{II} { 2.58	Si— O_{III} 1.64
O_{II} — O_{II} 2.63	Fe— O_{III} 1.97
O_{III} — O_{II} { 2.59	Ba— O_{III} 2.73
	Ba— O_{II} 2.98

The interatomic distances in Table 6 show excellent agreement with expected values. Ba is found to have eight-fold coordination.

The four-fold coordination of Fe is unusual for this element, but since the four oxygens are arranged in a square which is centered on the iron this is like octahedral coordination with a pair of opposite octahedron corners unoccupied. Such a coordination has not previously been reported for iron in silicates, but is known for several elements in other types of compounds. The arrangement of four (CN) groups in a square about Ni has recently been found in $\text{BaNi(CN)}_4 \cdot 4\text{H}_2\text{O}$.⁸

RELATED STRUCTURES

The mineral most closely related to gillespite in composition is the triclinic sanbornite, $\text{Ba}_2\text{Si}_4\text{O}_{10}$, with which it is found in California.⁹ Professor Rogers cautiously stated "It seems likely that sanbornite has a structure similar to that of micas and related minerals, though there is no direct evidence that it is pseudohexagonal." He then described a pseudohexagonal structure which he pictured as "probable." It may well be that sanbornite is pseudohexagonal even though closely similar to gillespite in composition. It has been shown that the roles of Fe and Ba in the gillespite structure are very different. Substitution of Ba for Fe to give the composition of sanbornite might be expected to result in a different linkage of the Si_4O_{10} sheets and possibly a different structure of the sheets themselves. A powder pattern of a triclinic mineral cannot be very illuminating, but at any rate, such a pattern made from sanbornite showed no similarity with powder patterns of gillespite.

So far as the writer is aware only one of the classifiers of silicate structures has included gillespite and sanbornite in his considerations. They were classed as "*anhydrous non-aluminum disilicates*" by Berman¹⁰ without benefit of x-ray evidence.

In the enumeration of possible silicate structures it is usually stated or implied that "tetrahedra combined by three solid angles" produce sheets of indefinite extent.¹¹ Though all known structures with three shared tetrahedron corners throughout are sheet structures there are other geometrical possibilities. One might have double rings of tetrahedra. If, for instance, two trigonal Si_3O_9 rings, such as occur in benitoite, were placed one upon the other and tetrahedron corners shared between

⁸ Brasseur, H., and de Rassenfosse, A., Structure cristalline des cyanures doubles de baryum a base de platine, de palladium et de nickel: *Bull. soc. fran. min.*, **61**, 129-136 (1938).

⁹ Rogers, *op. cit.*

¹⁰ Berman, H., Constitution and classification of the natural silicates: *Am. Mineral.*, **22**, (Palache number) 342-408 (1937).

¹¹ Schwartz, C. K., Classification of the natural silicates: *Am. Mineral.*, **22**, 1075 (1937).

them, a double ring, Si_6O_{15} , would result. Double rings of like Si/O ratio with three corners of each tetrahedron shared might also be tetragonal, hexagonal or pseudo-hexagonal. Such structures would not conflict with known requirements of ionic radii or tetrahedron linkage.

In some respects the structure of gillespite resembles that of apophyllite,¹² the formula of which is best written $\text{KF} \cdot \text{Ca}_4\text{Si}_8\text{O}_{20} \cdot 8\text{H}_2\text{O}$. There are two such units¹³ in the cell of dimensions $a = 9.00\text{\AA}$, $c = 15.8\text{\AA}$ and the space group is $D_{4h}^6 - P4/mnc$. The linkage of tetrahedra is similar to that of gillespite, there being two Si_8O_{20} sheets parallel to the base in each cell, with unshared tetrahedron corners pointing alternately upward and downward on either side of each sheet. The bonding of sheet to sheet, however, is quite different, involving also F and OH in the coordination about the positive ions.

LEACHING OF GILLESPIITE

Schaller¹⁴ reported that gillespite can be leached with the complete removal of iron and barium. The glistening flakes which remain are uniaxial negative like gillespite, but the mean index drops to about 1.45. The flakes take up a great deal of water and Schaller considered them, on the basis of quantitative determinations, to have changed in composition from $8\text{SiO}_2 \cdot 2\text{FeO} \cdot 2\text{BaO}$ to $8\text{SiO}_2 \cdot 2\text{H}_2\text{O} \cdot 2\text{H}_2\text{O} \cdot \text{H}_2\text{O}$. Assuming that the new material occupies exactly the same volume as the original its density would be expected to be 2.08. Any lower density would be indicative of loosening of the structure attending leaching or of swelling upon hydration.

The leaching experiments were repeated, confirming all of Schaller's observations, and the density of the colorless leached flakes was found to vary between 1.8 and 2.0, mostly near 1.9, showing that little, if any, swelling occurs. Under the circumstances one might expect to find the silicate sheet structure retained in the leached, hydrated material. Attempts to observe x-ray diffraction in the leached material by powder and rotation methods led to negative results, but a long exposure Laue pattern, made with the aid of an intensifying screen, with beam normal to the base of a well leached flake still shows a very faint tetragonal design (Fig. 5) on which half a dozen spots may be roughly measured in each quadrant. By contrast, over a hundred spots are measureable in

¹² Taylor, W. H., and St. Náray-Szabó, The structure of apophyllite: *Zeits. Krist.*, **77**, 146-158 (1931).

¹³ Not four, as stated by Bragg in *Atomic Structure of Minerals*, p. 227 (1937).

¹⁴ Schaller, W. T., The properties and associated minerals of gillespite: *Am. Mineral.*, **14**, 319-322 (1929).

one quadrant of a similar pattern made from fresh gillespite. At most only a faint trace of the structure of gillespite is retained in the leached flakes.

The leaching or "bleaching" of biotite by acid solutions, a process that also occurs widely in nature, has long been familiar to mineralogists. A recent study¹⁵ of the leaching of biotite has again shown that the fully

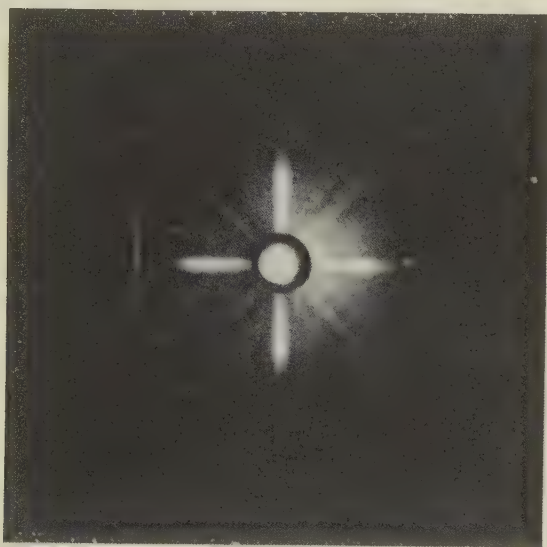


FIG. 5. Laue pattern of leached gillespite. Beam normal to 001.

leached material is amorphous to x-rays when examined by the powder method, as long ago reported by Rinne. While the flakes remain uniaxial negative their mean index drops as low as 1.43.

The writer has leached dark biotite from the Half dome quartz monzonite west of Tenaya Lake in Yosemite National Park¹⁶ with an initial density of 3.03 and mean index of about 1.65. The final leaching product gives no powder diffraction pattern, has a density of 1.7–1.8 and a water content (ignition loss) of nearly 11%.

Bailey¹⁷ has recently described apophyllite from California naturally

¹⁵ Mehmél, M., Ab- und Umbau am Biotit: *Chemie der Erde*, **11**, 307–332 (1937).

¹⁶ This is doubtless the same or nearly the same as the biotite analyzed by Hillebrand and reported by H. W. Turner, Some rock-making biotites and amphiboles: *Am. Jour. Sci.*, (4) **7**, 294–298 (1899), from "Tioga road southeast of Mt. Hoffmann."

¹⁷ Bailey, E. H., Skeletonized apophyllite from Crestmore and Riverside, California: *Am. Mineral.*, **26**, 565–567 (1941).

altered to a material which is largely hydrated silica and retains the uniaxial negative character of fresh apophyllite though its mean index is only 1.44. Others have previously described similar occurrences. Bailey supposes the apophyllite to have "undergone a selective leaching process" "without destroying the framework of the crystals." He also failed to observe *x*-ray diffraction by the powder method in the leached material.

It seems that changes produced by leaching in apophyllite, gillespite, and biotite with removal of cations and addition of water are very similar. The flakes retain their shape and some of their optical properties but yield no *x*-ray diffraction pattern when examined by the powder method.

NOTES ON CORDIERITE: (A) CORDIERITE CRYSTALS
FROM A GLASS FURNACE; (B) CORDIERITE
FROM HORNS NEK, TRANSVAAL

S. J. SHAND,
Columbia University, New York, N. Y.

(A) CORDIERITE CRYSTALS FROM A GLASS FURNACE

A group of cordierite crystals, recovered from the wall of a tank in which glass is manufactured, was given to me lately by a friend who requested that the name of the factory be withheld from publication. I am only permitted to state that the tank in which the charge is melted is composed of aluminum silicate, having nearly the composition of mullite; that the glass is a borosilicate variety containing magnesium; that the tank is heated by oil burners from above; and that the temperature at the hottest point may reach 1600°C. Under these conditions a crust of cordierite crystals was formed on the wall of the tank, a little distance above the top of the melt. I am assured that the glass never stood at such a high level as the crust, and creeping of the melt up the walls of the tank seems to be excluded because the wall is rather deeply undercut between the crust and the top of the melt. The suggestion has therefore been made that the magnesia required to convert mullite into cordierite may have been volatilized from the melt. (But the late Professor Peck, of Ann Arbor, offers the simpler suggestion that dust from the charge, settling on the wall of the tank, was the cause of the reaction.)

Cordierite has been synthetized, intentionally or accidentally, by several experimenters. The most recent synthesis was described by Dittler and Köhler in 1938.¹ Mixtures of magnesia, alumina, and silica in the proportions of 1:1:3, 2:2:5, and 3:3:8 were melted in magnesite crucibles, in a gas furnace at 1400°. The 2:2:5 mixture was found to give the best yield of cordierite, the others being contaminated with sillimanite and spinel. The pseudo-hexagonal crystals had the following properties:

$$\alpha = 1.524$$

$$2V(\alpha) = 50^\circ\text{--}57^\circ, \text{ mean } 53.5^\circ.$$

Crystals from the 1:1:3 melt had slightly different properties, namely

$$\alpha = 1.526$$

$$2V(\alpha) = 65^\circ\text{--}78^\circ, \text{ mean } 74^\circ.$$

An earlier synthesis of pure magnesia-cordierite was made by Rankin and Merwin² in 1918. The crystals gave interference figures which were

¹ *Centralblatt Min., Abt. A*, 149 (1938).

² *Am. Jour. Sci.*, 45, 301 (1918).

"nearly or quite uniaxial negative." Those formed from melts containing 66 per cent of silica had the following refractive indices:

$$\alpha=1.519, \beta=\gamma=1.522.$$

Crystals from melts containing about 50 per cent of silica showed

$$\alpha=1.524, \beta=\gamma=1.528 \pm .002.$$

Rankin and Merwin thought there was a possibility of solid solution, the crystals ranging in composition from 1:1:3 to 2:2:5.

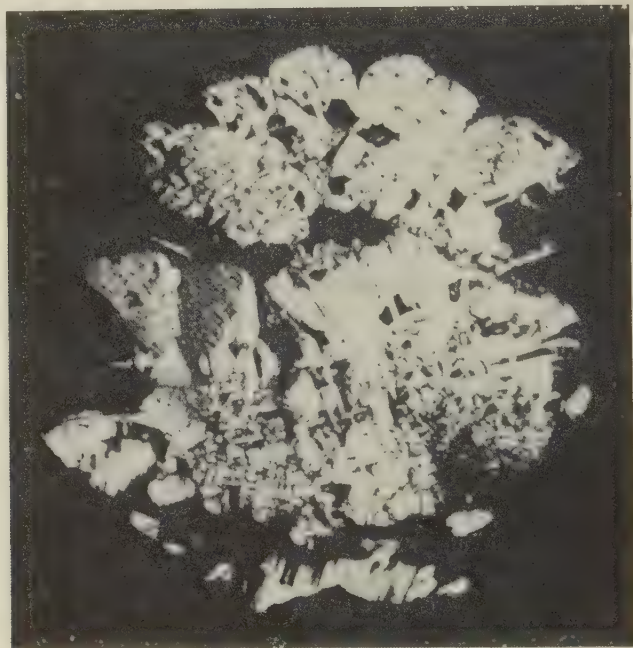


FIG. 1. Transverse section of a hexagonal prism of cordierite, between crossed nicols. Magnification 14 diameters. The prism is seen to be composed of six smaller prisms in contact, each of them showing sector twinning and complex intergrowth.

In view of the prevailing uncertainty regarding the composition of cordierite, and the relation between composition and optical properties, it seemed desirable to make a study of the crystals from the glass furnace. The specimen, measuring about $4 \times 2\frac{1}{2}$ inches, consists of an aggregate of water-clear crystals from 2 to 5 millimeters long, resting upon and growing out of a thin plate of scale from the wall of the tank. The crystals have the shape of hexagonal prisms, but each crystal is actually a group of similar prisms in nearly parallel position. A thin section made from

one of these groups proved, when examined between crossed nicols, to be a very complex aggregate in which the familiar sector twinning of cordierite is combined with quite irregular intergrowth (Fig. 1).

The optic axial angle was measured on the universal stage, using various sectors of the twinned crystal. The sign was always negative.

Refractive index of hemispheres, 1.554

$2V=82^\circ, 83^\circ, 82^\circ$.

Refractive index of hemispheres, 1.516

$2V=83^\circ, 82^\circ$.

I am indebted to Dr. E. N. Cameron for measuring the refractive indices of the cordierite, using the immersion method with variable temperature. He found

$\gamma=1.5270 \pm .0003$

$\alpha=1.5223 \pm .0003$

To determine the specific gravity, about 2 grams of broken crystals were weighed in a pycnometer. The result was 2.520 at $19^\circ\text{C}.$, which is equivalent to 2.516 at $4^\circ\text{C}.$

The crystals were now analyzed with the following result:

	%	mol. no.
SiO ₂	50.77	.846
Al ₂ O ₃	35.26	.345
CaO	1.24	.022
MgO	12.72	.318
H ₂ O	.25	
	100.24	

Iron is absent, the alumina precipitate being pure white after ignition. A flame test for boric acid, made with potassium bisulphate and calcium fluoride, gave no coloration. This test is said by Hillebrand to be sensitive to 0.2%. Considering the high temperature at which the crystals were formed, the water must be regarded as "moisture."

From the molecular numbers given in the second column it appears that the ratio of $\text{MgO}+\text{CaO}:\text{Al}_2\text{O}_3:\text{SiO}_2$ is almost exactly 2:2:5.

B. CORDIERITE FROM HORNS NEK, TRANSVAAL

In the year 1905, H. Kynaston³ described a curious rock from Horns Nek, a pass over the Magaliesberg range near Pretoria, and named it "nepheline granophyre." About a mile north of the Nek the norite of the Bushveld complex comes into contact with the slates and quartzites of the Magaliesberg series; and Kynaston described the gradual passage of normal norite into a marginal diabasic facies which contains some in-

³ *Trans. Geol. Soc. S. Africa*, 8, 60 (1905).

terstitial quartz and micropegmatite. The supposed nepheline granophyre was found in this passage zone. It is a dark, fine-grained rock consisting of quartz, feldspar, hypersthene, biotite, and rounded areas of fine, feathery micropegmatite. The mineral which was described as nepheline forms tiny idiomorphic prisms within the micropegmatite. Kynaston noted that this mineral shows quadratic and hexagonal cross-sections, a faint yellowish color, and "a lamellation suggesting a quadruple twinning." The identification of this mineral as nepheline, in spite of these unfamiliar characters, was based on a staining test which appeared to show that the mineral was gelatinized by acid.

When I read this description, some 20 years later, I was convinced that the identification of nepheline must be erroneous for the reason that nepheline is chemically incompatible, under magmatic conditions, not only with quartz but also with hypersthene. Dr. A. L. Hall kindly permitted me to borrow the original rock specimen from the museum of the Geological Survey, in Pretoria, and to cut a new thin section from it. In this preparation the little hexagonal grains, which average 0.5 millimeter in diameter, all show sector twinning between crossed nicols. There are commonly 4 to 6 roughly triangular sectors, each of which is optically biaxial. When the slide was treated with hydrochloric acid and malachite green this mineral was not affected at all, proving that it is not nepheline.

When studying the synthetic cordierite described in the preceding note I was reminded of the Horns Nek rock, and I re-examined the thin section on the universal stage. Several measurements of the optic axial angle in different sectors of the twinned crystals gave the following results:

$$2V(X) = 70^\circ, 68^\circ, 70^\circ, 72^\circ, 72^\circ, 70^\circ; \text{average } 70^\circ.$$

The plane of the optic axes, in each sector, is perpendicular to the prism face which forms the base of that sector. If any doubt remains that this mineral is actually cordierite it should be dispelled by the observation that the grains show progressive alteration to a green chloritic substance.

Further study of this thin section leads me to believe that even the name "granophyre" was wrongly applied to this rock. Instead of being a marginal facies of the norite, as Kynaston assumed from its occurrence in the marginal zone, I judge it to be a cordierite-hypersthene hornstone formed by thermal metamorphism of a siliceous slate. The feldspar in the micropegmatite is orthoclase; that in the darker part of the rock sometimes shows faint twinning lamellae, but wherever the relief could be observed it was less than that of canada balsam. Quartz occurs in interlocking grains. The distinctly pleochroic hypersthene is mostly in shapeless grains which are moulded on feldspar and quartz. Biotite has been formed at the expense of hypersthene. Of all the minerals present, cor-

dierite alone is idiomorphic. It is difficult to identify this mineral in the dark part of the rock, among the little grains of quartz, feldspar, hypersthene, and ore. No sector twinning could be detected in this part of the rock, so it is likely that cordierite is confined to the micropegmatite patches.

It is not often that one finds such abundant micropegmatite in a metamorphic rock, but I may refer to Harker's drawing of a recrystallized feldspathic sandstone from the island of Rum⁴ for an illustration of such a rock.

⁴ Metamorphism, p. 68, Fig. 21 B.

NOTES AND NEWS
GELATINCOATED SLIDES FOR REFRACTIVE
INDEX IMMERSION MOUNTS

H. W. FAIRBAIRN,
Massachusetts Institute of Technology, Cambridge, Massachusetts.

The purpose of this note is to call attention to the use of gelatin coated slides for refractive index immersion work, as advocated more than ten years ago by Vedeneeva and Melancholin.¹ These investigators made use of the gelatin coating on standard lantern slides to embed grains intended for oil immersion work. As this procedure involved processing of the photographic emulsion and cutting of the plates to a suitable size prior to their use as mounts, Eastman Research Laboratories, at the writer's suggestion, coated a few dozen standard petrographic slides with hardened gelatin for general testing. The results were highly satisfactory, and although recognition of their work is belated, it appears that Vedeneeva and Melancholin have made a substantial contribution to the oil immersion technique used so commonly on this continent. The following description of the method is largely taken from their paper, with some slight additions.

The procedure is simple. First determine with a sharp point which side of the slide is coated. Then apply a drop of water over the area where the grains are to be scattered. The writer finds a small dropping-bottle useful for this purpose. Shake off the water after a few seconds and immediately scatter the grains to be examined over the softened gelatin. As the position of the grains cannot be altered after emplacement on the gelatin, care must be taken that the sample is dry so that it will scatter evenly over the moistened area on the slide. Place in as cool a place as is available until the gelatin is set. If "dry ice" is used the setting will be practically instantaneous; otherwise five or ten minutes is necessary, depending on the temperature of the room. Test the hardness of the moistened area by running a sharp point across the contact into the unmoistened area. The embedded grains are next capped with a cover glass and immersed in a suitable refractive index oil. The mount is now ready for use. After examination with one oil, the grains may be studied repeatedly with other oils by discarding the cover glass and carefully washing off the used oil with carbon tetrachloride or other suitable solvent. The writer keeps a small wash-bottle by the microscope for this

¹ Vedeneeva, N., and Melancholin, N., The theodolite immersion method, etc., *Trans. Sci. Invest. Inst. Industry*, No. 503. *Inst. App. Miner.*, Paper 54, (1932), (Russian and English).

purpose. If the grains have been properly embedded, the washing entails practically no loss of material. The originators of the method found that gelatin is neutral to all the oils in current use and, as the coating is much thinner than the diameter of the grains used, no difficulty was experienced in obtaining the Becke and oblique illumination tests. Several mounts may be made at different places on a slide before discarding it.

The advantages of the method are fairly obvious. Use of the same mount for successive oils is not only economical of material, but permits re-examination of those grains originally found to be most favorable for determinative purposes. Beginners will particularly appreciate this feature as it shortens the search for useful interference figures. The tendency of platy grains to lie flat on the slide is also somewhat lessened. Where the universal stage is employed, much annoyance is avoided and time saved through fixation of the grain selected for orientation. Care must be exercised here to avoid detaching grains through pressure of the hemisphere. After mounting on the stage, the slide should never be shifted unless the hemisphere set screws have first been loosened. It has been found feasible to use ordinary mounting oil (petrolatum, nujol, etc.) underneath the object glass; the correct index oil must be used, however, between the cover glass and hemisphere.

The slides cannot be used for work with crystals easily soluble in water, or with any low-index immersion media which have water as a component. These are minor handicaps, however, and do not apply to the great majority of crystals.

Vedeneeva and Melancholin have also described a method for temporarily transferring a standard, balsam-mounted thin section to a gelatin-coated slide, with the object of determining refractive indices. The writer does not consider this a very practicable method, however, as the manipulation requires much care and several hours' treatment is needed to thoroughly remove the balsam. The mineral powder method, on the other hand, is simple, economical, and effective, and should be better known.

In anticipation of a demand for these slides, the Will Corporation of Rochester, N. Y., is undertaking to supply the 25×44 mm. size at 40 cents a dozen.

NOTES ON THE FELKER DI-MET ROCK SAW

H. W. FAIRBAIRN,

Massachusetts Institute of Technology, Cambridge, Massachusetts,

This small laboratory rock saw (Model 11-B),* which for several years has been available for geological work, is of more universal use than any other known to the writer at present. A wide range in specimen shapes and sizes can be successfully handled, and, as plasticene is used for mounting instead of rigid clamps, there is little damage to saw blades.

The makers advocate the use of oil rather than water in order to prolong the life of the blades. Although this is undoubtedly true in principle it is not a satisfactory procedure for plasticene mounting. Oil tends to dilute the clay and loosen the specimen beyond the safety point. As an alternative, two liberal streams of water, applied one on each side of the blade from small faucets, have been found superior in every respect. Upon changing specimens it is only necessary to remove with a cloth any water or rock fragments adhering to the surface of the plasticene.

Two manually operated drives have been added to the saw in use by the writer. One of these moves the specimen table, the other adjusts the height of the saw above the table. This latter drive is highly desirable as it permits gradual vertical adjustment while a cut is being made. It also makes vertically directed cuts possible in cases where the specimen shape is unsuited to the normal horizontally directed cut.

In order to make parallel cuts without shifting the specimen, a brass plate has been laid over the specimen table and held in place by bending its ends under the back and front of the table. The edges of the plate parallel to the sides of the sliding table are bent up so as to be easily grasped by the fingers. By making this plate an inch or so narrower than the specimen table, a small lateral movement is provided which is adequate for all ordinary work and saves considerable time where parallel cuts are needed. Construction of an elaborate lateral drive for this purpose would reduce the effective size of the specimen table and thus the general usefulness of the saw.

The addition of this plate necessitated the removal of the adjustable bars intended to aid in holding the specimen. It was found that these bars could be dispensed with entirely. Instead, the plate was scored with a sharp cutting tool, thus providing the plasticene with a roughened base. With large specimens it has been found advantageous to pound the plasticene into place around the base of the specimen with a hammer.

* Musto-Keenan Co., Sales Division, 1801 S. Soto St., Los Angeles, Calif. Also John Neu, Inc., 34-50 Vernon Blvd., Long Island City, N. Y.

This is more rapid than use of the fingers alone (particularly if the plastic is stiff) and insures adequate binding of the specimen to the saw table.

The improved saw as just described has the great advantage of flexibility of use without encumbrance by too many mechanical features. In commercial work where a uniform product is being cut and precision is necessary, as in quartz crystal processing, the use of goniometric devices and an automatic hydraulic drive is undoubtedly justified. For general purposes, however, these are unnecessary and add greatly to the initial cost and maintenance of the machine.

PROCEEDINGS OF SOCIETIES

PHILADELPHIA MINERALOGICAL SOCIETY

The Academy of Natural Sciences of Philadelphia Dec. 3, 1942

A stated meeting was held in the library of the Academy of Natural Sciences on the above date with Dr. Hersey Thomas presiding. Mr. Henry E. Millson gave a lecture on "Fluorescence and Phosphorescence of Minerals and other Materials" which was illustrated by a number of Photochrome lantern slides. These slides compared side by side minerals taken in white light and in ultra violet. Mr. Millson also displayed a series of polished minerals lighted by a 72-inch cold quartz light. A demonstration was also given on how phosphorescence and fluorescence are being used by war industries and for war purposes during blackouts. Mr. Trudell described a trip taken by the Society to Easton, Pa. on Nov. 15.

Jan. 7, 1943

Dr. Hersey Thomas presided, with fifty-eight members and visitors in attendance. Mr. Felix B. Shay of the Foote Mineral Co. gave a lecture on "Ilmenite, Rutile and Zircon." Mr. Shay described the commercial uses of these minerals and their occurrences as ores. A series of lantern slides were shown illustrating the different methods of mining and separating these minerals. Charles Toothaker displayed an interesting suite of crystals of rutile, brookite and octahedrite from several localities. Harold Arndt reported on a trip with the secretary on Jan. 2 to an asbestos mine near Rosetree, Del. Co., located on the estate of P. F. Biddle. Asbestos and anthophyllite were found intermixed in serpentine.

Feb. 4, 1943

Dr. Hersey Thomas presided, with fifty-two members and visitors present.

Mr. George D. Cremer of the Hardy Metallurgical Co. of New York gave a lecture on "Powder Metallurgy" which was illustrated by a number of lantern slides. The deaths of Harry Warford and Edward Allen were announced.

J. S. FRANKENFIELD, *Secretary.*

BOOK REVIEW
PRISM AND LENS MAKING
A TEXT BOOK FOR OPTICAL GLASSWORKERS

F. TWYMAN, F. Inst. P., F.R.S., Managing Director Adam Hilger Ltd., Pp. 178+iv, Figs. 70, $14\frac{1}{2} \times 22$ cm., cloth. Published by Adam Hilger Ltd., London, 1942. Price \$4.50. Obtainable in U.S.A. from the Jarrell-Ash Co., 165 Newbury St., Boston, Mass.

This book marks a departure from the traditional reticence of optical manufacturers to reveal their methods. It is the first thorough account to originate from a commercial source. May other manufacturers follow this praiseworthy example!

Following a short scholarly historical introduction, the elements of single lens working are taken up; the basic nature of the processes of grinding and polishing are discussed, as are also tools and materials for these operations. The production of lenses and prisms in quantity is next considered including detailed descriptions of the methods of assembling and working these in "blocks." It is here preeminently that an account from an outstanding manufacturer is of great value. Closing chapters are devoted to the testing of optical glass and of finished parts. Among the interferometers described for such testing is the well-known one invented by the author during the first world war which bears his name.

The book is a valuable contribution in a field in which literature is scant. It is primarily an account of the methods used by Hilger Ltd. It is of interest to both the beginner and the experienced optical worker. The restricted compass however precludes that it be encyclopedic in nature. The beginner needs further aid in the fundamental operations, especially in regard to the working of single surfaces by hand. And the experienced technician may with profit familiarize himself with methods of testing of which no account is here included. But for the considerable material which the book contains it is highly recommended.

CHARLES F. MEYER,
University of Michigan

NOTICE TO MEMBERS OF THE SOCIETY AND CONTRIBUTORS
TO THE JOURNAL

Due to the diversion of many of our contributors from teaching and research to pursuits relating either directly or indirectly to the war effort, there has been a marked decrease in the number of contributions submitted for publication. It is therefore necessary to announce a change in the issuing dates of the Journal.

After July 1 and possibly continuing for some time *The American Mineralogist* will be issued every two months instead of monthly. For the balance of 1943 there will be three issues instead of six: July-August (Nos. 7 & 8); September-October (Nos. 9 & 10); and November-December (Nos. 11 & 12).

Our members and subscribers are assured that as soon as conditions will permit we will again return to our normal policy of issuing a monthly periodical.

The first paper conservation order of the War Production Board affected only those periodicals which required more than 100 tons of paper per year. A supplementary order, recently issued, directs the publishers not affected by the first order, to limit paper consumption for 1943 to the amount used in 1942.

War Production order L-291, effective May 25, 1943, forbids the use of stitching wire in pamphlets containing twelve pages or less, including covers. Pamphlets of this size must be made up in newspaper form: unstitched. Restrictions are also placed on the number of stitching wires permitted for pamphlets containing more than twelve pages.